UNIVERSITY OF TORONTO

DEPARTMENT OF CHEMICAL ENGINEERING
AND APPLIED CHEMISTRY

OPERATION OF A
[illegible]CADE AUTOCLAVE
TO STUDY THE
LIQUEFACTION OF WOOD CHIPS

RENEWABLE ENERGY BRANCH

89-05648/

OPERATION OF A CASCADE AUTOCLAVE TO STUDY THE LIQUEFACTION OF WOOD CHIPS

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PREPARED FOR:

Bioenergy Development Program
Renewable Energy Branch
Energy, Mines and Resources Canada
Ottawa, Canada
DSS Contract File No: 38 ST. 23216-6-6346
Submitted 88 02 16

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1.1 ACKNOWLEDGEMENT

B.C. Research performed all the elemental analyses of our oil samples and determined total organic carbon contents of the aqueous phase products. Special thanks are due to Jim McKinley of B.C. Research who showed great interest in all our product analyses, and in particular, the proton and carbon-13 NMR spectra of the oil and aqueous phase organic products.

Stephen Allen, a graduate student of the Department of Chemical Engineering and Applied Science, University of Toronto, measured the apparent molecular weight of the oils using high performance size exclusion chromatography (HPSEC).

We thank the Scientific Authority, R. Douglas Hayes, for his interest and support.

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CITATION

Boocock, D.G.B. and Chowdhury A., Operation of a Cascade Autoclave to Study the Liquefaction of Wood Chips; Report of Contract File No. 38ST. 23216-6-6346. Renewable Energy Branch; Energy, Mines and Resources Canada, Canada 1988 (p 80).

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1.2 PREFACE

The work reported here was performed during the period November 1986 - October 1987 on the liquefaction of poplar wood chips and dowels in a cascade reactor. Modifications made to the original unit are outlined and results of 27 runs are tabulated and discussed.

Although the ultimate objective is to develop a continuous process for the production of oil using poplar or other wood as raw material, the objective of the present study is the identification and optimization of important process variables by the collection and analysis of experimental data from the operation of the "batch cascade" autoclave system.

The system is, we believe, the first designed specifically to liquefy wood chips using steam alone at high temperatures. This is significant since cost considerations preclude the use of dry powdered woods. It should be emphasised however, that the use of chips will have other economic effects, not all of which will be beneficial. For example, special feed system for chips will be required. However, this study does show that poplar chips offer little resistances to heat and mass transfer. Needless to say, not enough is known about the process at this time for the purpose of a full economic analysis of a continuous liquefaction unit.

The report will be of interest to those in the field of thermal biomass liquefaction, since it illustrates that commercial-sized wood can be liquefied using steam at sufficiently high temperatures. The present liquefaction unit has limitations in that it has a relatively small steam generator, and operates in a batch mode.

1.3 ABSTRACT

The objective of this year's wood liquefaction experiments in the cascade reactor was to identify important operating parameters, e.g., wood size, steam temperature and reaction time, and their effects on the products.

The 600 mL cylindrical reactor vessel, supported vertically, is preheated prior to a run. In operation, a mesh basket containing wood chips or dowels is introduced through the upper ball-valve to the nitrogen-purged reactor. After the closure of this inlet valve and the nitrogen purge valve, steam is immediately injected. The steam valve is closed (after approximately 5 seconds) and the reaction continued, usually for 2 minutes. At the end of the reaction time the contents are discharged into a cooling lock. The reaction time, three reactor temperatures and reactor pressure are recorded simultaneously in a data acquisition system.

Similar oil yields (w/w) were obtained with runs using steam temperatures[+] in the range of 335 to 355 ^{o}C and reaction times between 45 and 180 seconds. The average weight percent yield of oil (acetone-soluble product) was 43.1 %. The oil contained 58.7 % of the product carbon. The apparent number and

weight average molecular weights of oil were 600 and 1400 respectively. With time, the oil slowly polymerized. The carbon-13 NMR study shows that the aqueous phase contains a large number of organic compounds, the major one being acetic acid.

+ Throughout, "steam temperature" refers to the temperature in the steam generator. The temperature of steam entering the reactor is cooler due to adiabatic expansion. The mass yields were only calculated for the "oil" product.

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1.5 EXECUTIVE SUMMARY

The successful operation of the wood liquefaction unit has been continued, to produce acetone-soluble product from poplar chips. The main objective of these runs was to determine the effect of steam temperatures, poplar wood size and reaction times on the products.

For a particular run, a mesh basket containing IEA wood chips or dowels was inserted into the nitrogen-purged preheated reactor. The reactor's inlet, outlet and vent valves were closed, and steam was injected for a desired span of time (usually 5 seconds). After a short period of reaction time, the contents of the reactor were cooled in the product let-down lock and then discharged into the product receiver. The acetone-free product, solid at room temperature, could be readily separated from the aqueous phase. The volume of gas produced was determined using a water displacement system.

Temperatures at the top, middle, and bottom of the reactor were recorded with a computerized data monitoring and acquisition system. The products were received as acetone-free product, acetone-wash product (recovered from acetone used to clean the reactor and feed basket), an aqueous phase containing soluble

organics and suspended solids, acetone-insolubles (char and unconverted material not soluble in acetone), and gases.

Those aqueous phase suspended solids which were soluble in acetone were classified as part of the oil. The remaining acetone-insoluble aqueous phase solids were included in the unconverted material. Carbon contents and balances (11 runs) were determined from the elemental analysis of oils, acetone-insolubles, gases, and carbon content of the aqueous phase. The oil consisted of approximately 69 % carbon, <6 % hydrogen, 25 % oxygen, and traces of nitrogen.

The conclusions derived from the present study are as follows:

(a) The yield of oil was insensitive to steam temperature and reaction time in the ranges 335-355 ^{o}C and 45-150 seconds respectively. Runs with lower steam temperatures and reaction times produced more aqueous phase solids which were partly soluble in acetone. The aqueous phase solids were mostly partially converted lignin.

(b) The weight percent yield of oil was 43.1 % (δ= 3.9 %). The oils contained 58.7 % (δ= 0.9 %) of the product carbon (the carbon balance between feed and products was usually within 5 %). The remaining product phases, namely acetone-insolubles, aqueous phase organics and gases, contained 5.4 % (δ= 1.3 %), 29.5 % (δ= 1.5 %), and 6.4 % (δ= 0.9 %)

respectively of the feed carbon.

(c) In the cascade autoclave approximately 300 mL of aqueous phase was collected when 95 (± 5) g of wood chips were used. When 160 g of wood dowels were used, the amount of aqueous phase only increased to 320 mL and a higher oil yield (50 %) was obtained. It is concluded that the conditions in the reactor after steam injection (e.g. level of condensed water in the reactor, and reactor wall temperature) are important parameters governing the liquefaction.

(d) Wood chips were not liquefied completely even with prolonged reaction time (4 min) when less than 1 L of water was originally present in the 2-L steam generator. This phenomenon has been explained in the discussion.

(e) With time, the oil slowly polymerized, but the average molecular weight did not increase dramatically. Storage in THF did not prevent repolymerization. The apparent number and weight average molecular weights of oil were found to be 600 and 1400 respectively.

(f) Carbon-13 nuclear magnetic resonance revealed that there were numerous organic compounds present in the aqueous phase. The same analytical method also indicated lignin as the major precursor of the oil. The laboratory analysis

showed that the dissolved organics in the aqueous phase are glycolic, formic, acetic, and propionic acids.

More studies, using higher (3 cm diameter, 54 cm long) volume wood dowels (less void space) as feed material should be continued to verify conclusion (c) above. The system should be upgraded by further insulating the reactor top and bottom valves and their operators so as to further reduce heat loss during operation.

1.6 RESUME

2.1 INTRODUCTION

This study is the continuation of previous work on the liquefaction of poplar wood chips in a cascade reactor using steam at high temperature and pressure (Ref. 1). The present concept of wood liquefaction has been developed from a laboratory-scale study in which single wood sticks and cold water both were subjected to fairly rapid (2 to 3 minutes) aqueous pyrolysis inside a small tube type reactor, resulting in complete conversion to acetone-soluble product (oils), aqueous phase organics, and gases (Ref. 2).

The design of the wood liquefaction unit, procurement of the component parts, construction and trial operations were presented and described in the final report for 1985 (Ref.3). The study was continued to identify the relevant process variables (see Ref. 1). In the current report, we present the optimization of those variables and the analysis of other important factors involved in the process (e.g., aqueous phase products, wood geometry, etc.).

The following modifications were made to the unit:

(1) The old product let-down lock (122 mL) was replaced with a larger stainless steel vessel (300 mL) in order to accommodate all the oil and aqueous products from each run.

(2) The manual data collection procedure was inefficient and inconvenient considering the short reaction time involved. An automatic data acquisition system was installed so as to ease the recording and storage of temperature and pressure data.

(3) The high pressure Autoclave Engineering (AE) port valve for product discharge was replaced with the original Crosby ball-valve (now repaired and leakproof). Although the AE port value had a higher temperature and pressure rating, the internal geometry caused some product retention and occasional blocking.

2.2 OBJECTIVES

The objectives of this year's study on wood liquefaction were as follows:

(1) To optimize steam temperature and reaction time so as to minimize aqueous phase solids (partially converted wood) and maximize oil yields,
(2) To determine oil yields (w/w) and the carbon distribution in the products, and
(3) To determine the effect of wood particle size on the products.

2.3 METHOD

2.3.1 EQUIPMENT

The liquefaction unit consists of the following integral component parts:

(a) a steam generator (2 L)
(b) a cascade reactor (0.65 L, 1.5 inch I.D.)
(c) a reactor inlet ball-valve (1.5 inch I.D.)
(d) a reactor outlet ball-valve (0.5 inch I.D.)
(e) a product let-down lock and cooler (0.3 L)
(f) control panel and safety system
(g) a data acquisition system
(h) a product collector (2 L)

The complete liquefaction unit is shown schematically (not to scale) in Figure 1.

(a) The Steam Generator

The generator is a two liter (Autoclave Engineering) vessel capable of holding steam at or above 350 ^{o}C. The steam transfer line, from the autoclave top flange, passes vertically to a three way air operated valve. This valve has two open ends and a closed end where the steam line is connected. The steam/ nitrogen distribution line separates into three injection lines. The nitrogen purge line, which has an air operated valve,

Liquefaction Unit

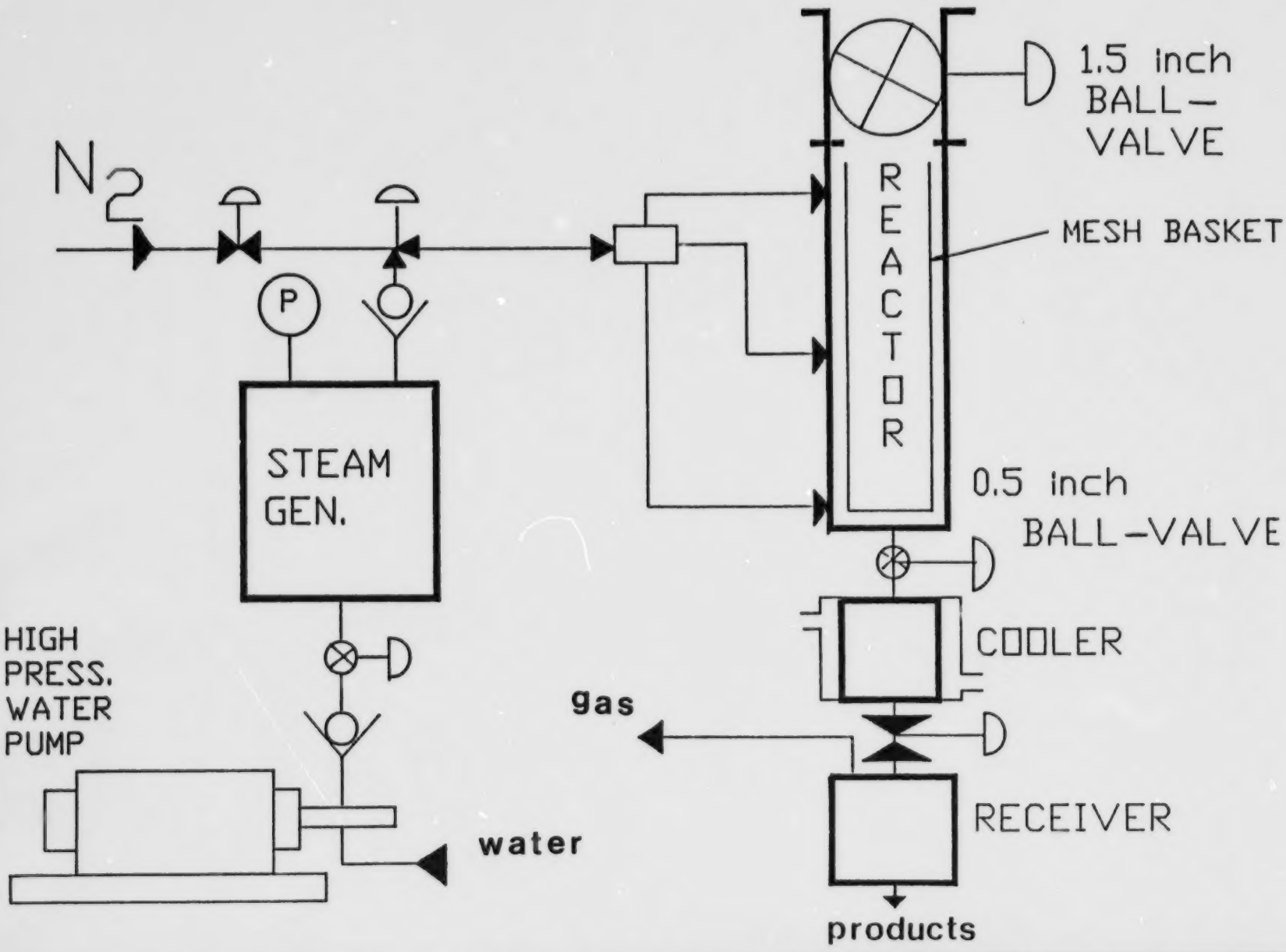


Figure 1

is connected at the one open end of the 3-way valve. Presently, the steam generator is being filled manually with water.

(b) Reactor

The reactor is an ss-316 vessel, 1.5 inches (3.81 cm) I.D, 3 inches (7.62 cm) O.D., and 21 inches (53.34 cm) long, capable of holding in it a cylindrical mesh basket containing 100 grams of wood chips. The reactor is rated for 3500 psi (24.1 MPa) at 350 ^{o}C.

The reactor is provided with eight holes to take 1/4 inch AE slim line connectors and one hole for 1/4 inch NPT connector. In use, the three holes on the left-hand side (when facing the reactor) are used for steam/nitrogen lines. The middle hole (1/4 inch NPT) on the front face and the bottom and top holes on the right side are used for thermocouples (1/8 inch). The upper hole on the front face is used for a rupture disc (3000 psi, 20.67 MPa), and the middle hole on the right-hand side is used for a pressure gauge. The remaining hole is used for venting the reactor.

The reactor is supported near its base by a split ring, spot welded to a support plate. This ring also supports a metal plate on which the reactor insulation, in the form of ceramic brick, is stacked up to the neck of the reactor. The brick is cut and fitted to the external contours of the reactor.

The reactor is heated by two six feet long (1/8 inch O.D.) heaters joined in parallel. These are coiled around the reactor, and held close to the reactor by four steel strips and eight circlips. The maximum power drawn by the heater is 4 KW. The coils are operated through a temperature controller. With all lagging in place, the reactor can be brought to a temperature of 365 ^{o}C in seventy minutes.

(c) The Inlet Valve

The inlet valve is a 1.5 inch (3.8 cm) I.D. Mogas ball-valve type (ANSI # 2500 Series) and is rated at 3600 psi (24.8 MPa) at 370 ^{o}C. The valve is joined to the reactor by a matching "Oteco" hub and is supported on the frame by two brackets. The valve controller is air operated via a solenoid valve. The valve and the controller weigh 68 kilograms and are attached to a pulley system to facilitate removal from the reactor if required.

The valve is insulated from excessive heat loss by three layers of 1.5 inches (3.8 cm) thick glass wool. Thus, heat losses are limited primarily to conduction through the inlet port and controller.

(d) Reactor Outlet Valve

The outlet from the reactor and inlet to the product cooler are connected by a Crosby 0.5 inch I.D. ball-valve. It is rated

2650 psi at 700 $^{o}_{F}$ which is above the normal operating conditions of the cascade reactor. The previously used reactor outlet valve (AE Port Valve) easily held pressure. However, the internal geometry of the port valve caused some product retention and eventual blocking. The heavy-duty Crosby ball-valve had previously been installed with the help of a specially fabricated mounting device so as to avoid any damage to the seats. However, the valve started leaking when initially installed. It was subsequently found that one of the seats had been damaged due to a faulty mounting device. The valve was then sent to THP Inc. for repair, and has been working leak-free since its reinstallation.

(e) Product Let-down Lock

The volume of product aqueous phase and oil was found to be much higher than originally anticipated. Because of the size of the original let-down lock (122 mL), all the products could not be removed in one discharge. To alleviate this problem, a 300 mL stainless steel vessel having a cooling jacket was ordered from THP Inc., Montreal. It is a 15 cm long and 5 cm I.D. vessel, and rated at 13.8 MPa (2000 psi). It is provided with three ports. One of the ports is for a pressure gauge line connection and the other two ports are for thermocouples to measure temperatures at the top and bottom of the vessel.

The jacket of the let-down lock is connected to the low pressure steam line, and the passage of steam keeps the inside

temperature of the lock from falling below 96 ^{o}C. This assists the flow of the oils and aqueous phase products into the product receiver. The low pressure steam line can be replaced with the standby hot or cold water lines, if necessary.

(f) Control Panel and Safety System

The control panel is located in a room adjacent to the unit. The panel contains main switches as well as switches to open and close various valves. A single digital readout only allows the read out of one thermocouple at a time - as determined by the multiposition switch mounted on top of the control panel. There are three temperature controllers connected to the control panel; one each for the steam generator and reactor heaters, and one for the solenoid valve which controls the cold water flow to the cooling coil of the steam generator (upper temperature control).

The unit is located inside an explosion proof room. To avoid any accident due to sudden release of steam, the equipment has been provided with an electrical override, workable with the help of an electromechanical device. The equipment is also designed such that, (a) the main inlet valve cannot be opened if the steam inlet is open, and (b) the bottom product discharge valve cannot be opened when the reactor outlet valve is open and vice versa. The override does not, however, prevent the accidental discharge of the reactor contents to the atmosphere. To avoid this possibility, the main inlet valve is

a keyed switch and can only be operated if the key is inserted.

Finally, `Plexiglas' sheeting is installed in locations where sudden leaks could expose operators to high temperature and pressure steam.

(g) Data Acquisition System

It was proposed and recommended in the annual report for 1986 that the system be upgraded to allow continuous recording and storing of pressure and temperature during each liquefaction run. A data collection and handling system acquired for this purpose is comprised of: (1) a pressure transducer and thermocouples, and (2) a computer with a data acquisition and control interface board (Dash-8). Dash-8 is connected to a Universal Analog Input and Expansion Sub-Multiplexer (EXP-16) and a Labtech Notebook (LNT-03). The system is equipped with a monitor and a Roland 1212 printer.

(1) A pressure transducer is necessary to record the reactor pressure during each experiment having usually a short reaction time. The pressure sensor procured (type P741-0001) is a Schaevitz, England, product and has a range of 0-3500 psi absolute. Arrangement is made to join this device to the bottom end of a T-fitting connected to the reactor pressure line. A pressure gauge mounted on the top of the tee will give visual pressure readings. The sensing device will be mounted vertically and attached via a stainless steel U-tube

line to the bottom of the T-fitting. The U section of the tube will be dipped into cold water to avoid temperature shock of the sensor diaphragm which is rated only at 100 ^{o}C. A 10 Volts DC regulator is required to operate this transducer. Five ceramocouples (three for reactor top, middle and bottom, and two for product cooler top and bottom), each made of J-thermocouples, are connected to the universal analog input and sub-multiplexer (EXP-16) for temperature measurements.

(2) The computer supplied by Ultinet Business Systems of Toronto is an IBM XT compatible and was provided with a 5150 keyboard, two 360 DSDD disk drives, serial and parallel ports, clock/calendar card, and 640 k Ram. A data acquisition and control interface board (Dash - 8) is connected to the computer set.

The Dash-8 is an 8 channel, 12 bit successive approximation A/D converter with sample/hold. The full-scale input of each channel is +/- 5 volts with a resolution of 0.00244 volts. The A/D conversion time is typically 25 microseconds. The applications of Dash-8 include data logging, process control, signal analysis, energy management, product testing, digitizers and touch screens, laboratory and medical instrumentation.

To extend the capabilities of Dash-8, two expansion modules, namely an Expansion Multiplexer and Instrumentation (EXP-16) and a Labtech Notebook (LNT-03) are connected via a flat insulation displacement cable to the 37 pin Dash-8 I/O

connector.

The EXP-16 multiplexes sixteen differential inputs to a single analog output suitable for connection to any of the analog input channels of Dash-8. EXP-16 boards are cascadable so that up to eight EXP-16 boards can be attached to a single Dash-8 providing a total of 128 channels. The expansion multiplexer board includes a low drift instrumentation amplifier with preselected switchable gains of 0.5, 1, 2, 10, 50, 100, 200 or 1000. A cold junction correction sensor is also included for software compensation of thermocouples which can be directly connected to EXP-16.

The Labtech Notebook, a software package, performs many functions of the laboratory using a single set of tools. Some of the important functions are: data acquisition and process control, storage and screen display of experimental data, and data manipulation and curve fitting. All commands are menu driven and there is no need to remember command names or sequences. Data files generated by Labtech Notebook are formatted for direct link to LOTUS 1-2-3 providing the full analytical power and graphing functions of LOTUS to data reduction.

(h) Product Receiver

The outdated 1 L product receiver has been replaced with a 2 L heavy-duty pyrex glass vessel so as to accommodate the higher

pressure surge expected from the new and larger product let-down lock. The inlet line of the receiver is connected to the let-down lock through a 1/4 inch AE port valve. One of the two outlet lines of the receiver is connected to a bottom valve for aqueous phase and oil collection, while the other line, at the top, is attached to the vent or gas collector line. A third line at the top of the product receiver is attached to a rubber tubing closed at the end. This is a safety device which is designed to burst in the event of excessive incoming gas pressure. The outside body of the glass vessel is wrapped with duct tape to minimize damage in case of structural failure. From the operational safety point of view, the surge of pressure is controlled by repeated and very short on and off operation of the product discharge valve (1/4 inch AE port valve). Personnel are not allowed in the reactor room during discharge of products.

2.3.2 MATERIALS

International Energy Agency (IEA) poplar wood (clone D38) chips were used as feed material for most of the runs. The chips contained 8.5 % moisture, 47.31 % carbon, 6.04 % hydrogen, 43.52 % oxygen, and 0.14 % nitrogen. Two experiments were done using poplar wood dowels (1.25 inches diameter and 4 inches long). The elemental compositions of the dowels and poplar chips were assumed to be the same.

2.3.3 OPERATION

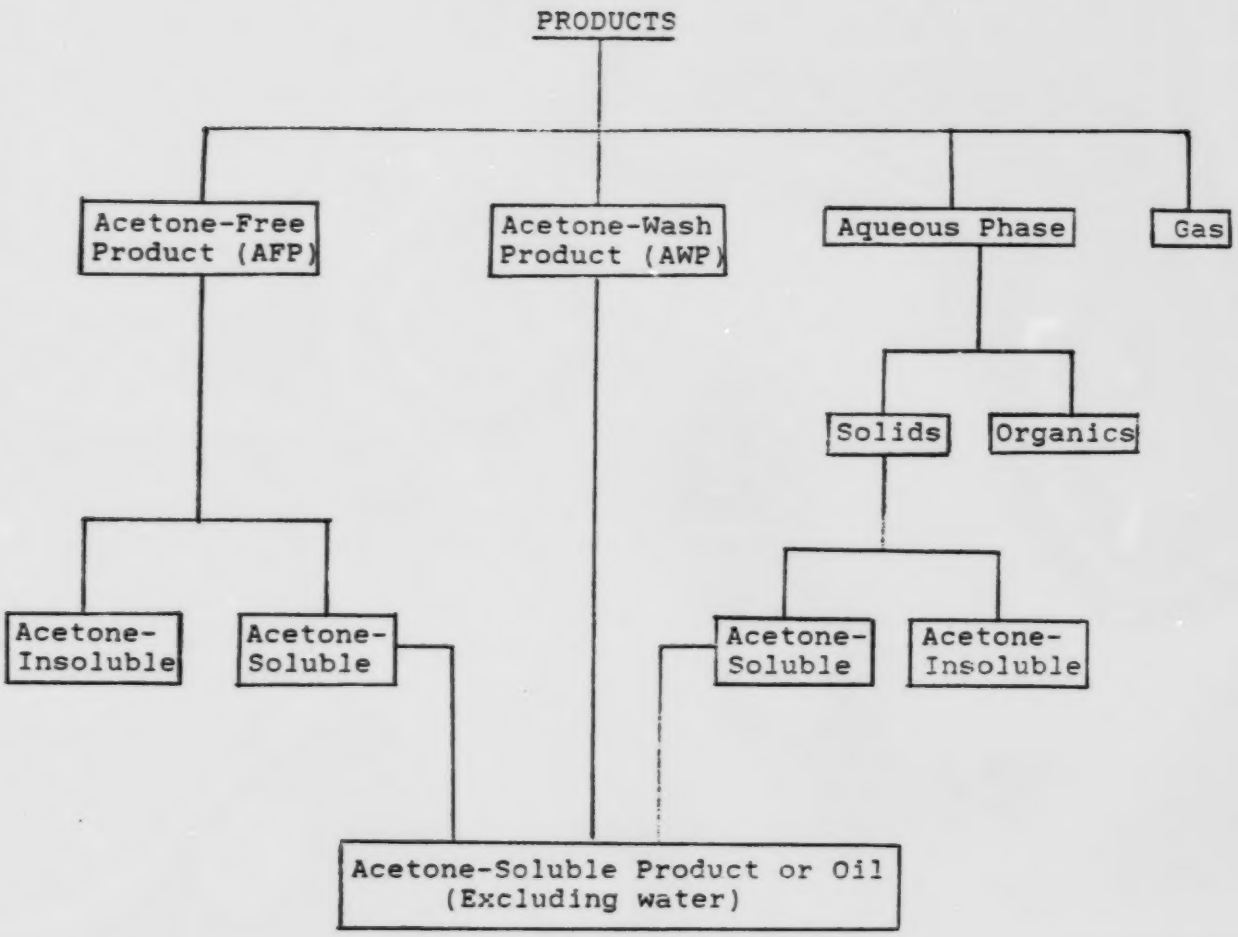
A mesh basket was filled with approximately 100 grams of IEA wood chips or 160 grams of wood dowels. With the steam generator temperature raised to the desired point (330 - 355 ^{o}C) and the reactor temperature at 400 - 410 ^{o}C, the basket was inserted through the reactor inlet valve to the nitrogen purged reactor. Care was taken to ensure that the basket cleared the rotating ball of the valve. The nitrogen flow was stopped. The inlet valve was closed and steam immediately was injected (usually for 5 s). After the reaction time (usually 2 minutes), the products were discharged through the outlet ball-valve to the product let-down lock where low pressure steam was circulating through the cooling jacket. After approximately 30 seconds the lock outlet valve was opened and the products flowed into the product receiver. The product collection cycle was repeated as many times as necessary and the unit cooled. A water displacement system connected to the product receiver was used to measure the volume of the gas produced.

The reactor, lock system, and basket were washed with acetone to recover any remaining products and then weighed to quantify adhering residue. After the acetone wash the basket was removed from the reactor using a hook.

2.3.4 Product Separation and Analysis

The major products obtained were acetone-soluble product (oil) (derived from acetone-free product, acetone-wash product, and aqueous phase solids), aqueous phase, acetone-insolubles, and gases. The relationships between the various product phases are shown in a diagram on page 15. The acetone-free product, on cooling, solidified and separated from the aqueous phase. It was dried overnight in a water-aspirated dessicator to lower moisture content below 20 %. The aqueous phase was centrifuged to recover the aqueous phase solids. Products that were not discharged were recovered by washing the unit with acetone. The acetone wash was then filtered through a 150 mL fritted glass filter of course grade. The acetone-wash product was recovered by evaporating the acetone in a Buchi Rotary Evaporator at 60 -70 ^{o}C under vacuum.

Moisture content of the oils was determined using a Karl Fisher automatic titrator. Elemental (carbon, hydrogen, oxygen, and nitrogen) analyses of the oils and carbon content of the aqueous phase organics were performed by B. C. Research, Vancouver.


PRODUCTS
Acetone-Free Product (AFP)
Acetone-Wash Product (AWP)
Aqueous Phase
Gas
Solids
Organics
Acetone-Insoluble
Acetone-Soluble
Acetone-Soluble
Acetone-Insoluble
Acetone-Soluble Product or Oil (Excluding water)

2.3.5 RESULTS AND DISCUSSION

This section covers the following aspects of wood liquefaction: oil yields, aqueous phase solids, optimum reaction time and steam temperature, larger wood sizes, molecular weight distribution of the oils, and nuclear magnetic resonance of oil samples and aqueous phase organics. Of the 30 runs performed this year, 27 are compiled in the report.

To help the reader better understand the discussion based on this years's results, the major findings compiled in the previous report are presented as follows (Ref. 1):

(1) steam temperatures below 335 ^{o}C resulted in incomplete conversion of the wood chips,

(2) increasing the steam temperature from 335 to 355 ^{o}C decreased the yield of acetone-insolubles and aqueous phase solids, while the amount of collected aqueous phase increased,

(3) decreasing the volume of water in the steam generator increased the yield of acetone-insolubles and sometimes caused incomplete conversion,

(4) the product distribution is dependent on steam temperature, steam injection time, initial temperature of the reactor, reaction time, and water level in the steam generator, and

(5) the acetone-soluble oil contained approximately 70 % carbon, 6 % hydrogen and 24 % oxygen, and softened around 50 ^{o}C.

A summary of the operating conditions, product masses, and the temperature/pressure profiles of the experiments are presented in Appendix 1. The temperature/pressure profiles of the unit during each run were discussed in detail in a previous report (1986). Appendix 2 shows the elemental analysis of the products, the carboxylic acid content of the product aqueous phase, the total carbon content in the products, and the percent carbon distribution of product phases. The pie charts in Appendix 2 illustrate the percent carbon distribution in the products.

The oil yield, reaction time, and steam temperature of 25 experiments using wood chips as feed material are presented in Table - 1. The results show that the oil yield from most of the runs (18 out of 25) lie in the range of 40 to 45 % (w/w). The average of the remaining seven runs is 46.6 %. Previous experimental results (1986 report) showed similar oil yields.

Temperatures of 400 ^{o}C for the upper part of the reactor and 290 ^{o}C for the lower section (before steam injection) were sufficient to cause conversion of the wood chips. Temperatures below these values resulted in the accumulation of more water in the reactor and incomplete conversion of the chips. Presently, even reactor higher initial temperatures are being used for wood liquefaction studies. The results will be incorporated in a future report.

Seventeen of the 25 experiments, as mentioned in Table - 1,

Table - 1 SUMMARY OF EXPERIMENTS

Run #	Steam Temperature (^{o}C)	Reaction Time (seconds)	Oil Yield % (w/w)
1	350	90	41.2
2	350	120	51.9
3	350	150	43.7
4	350	120	38.8
5	350	120	44.3
6	350	90	51.7
7	350	180	50.9
8	350	150	45.7
9	350	120	49.8
10	350	120	42.9
11	350	90	41.3
12	350	90	42.6
13	350	60	42.7
14	350	45	47.5
15	350	45	39.6
16	350	120	42.7
17	350	120	39.8
18	355	120	35.7
19	340	120	42.6
20	340	150	43.0
21	340	120	41.0
22	340	180	42.2
23	335	120	42.5
24	345	120	41.8
25	355	120	41.8

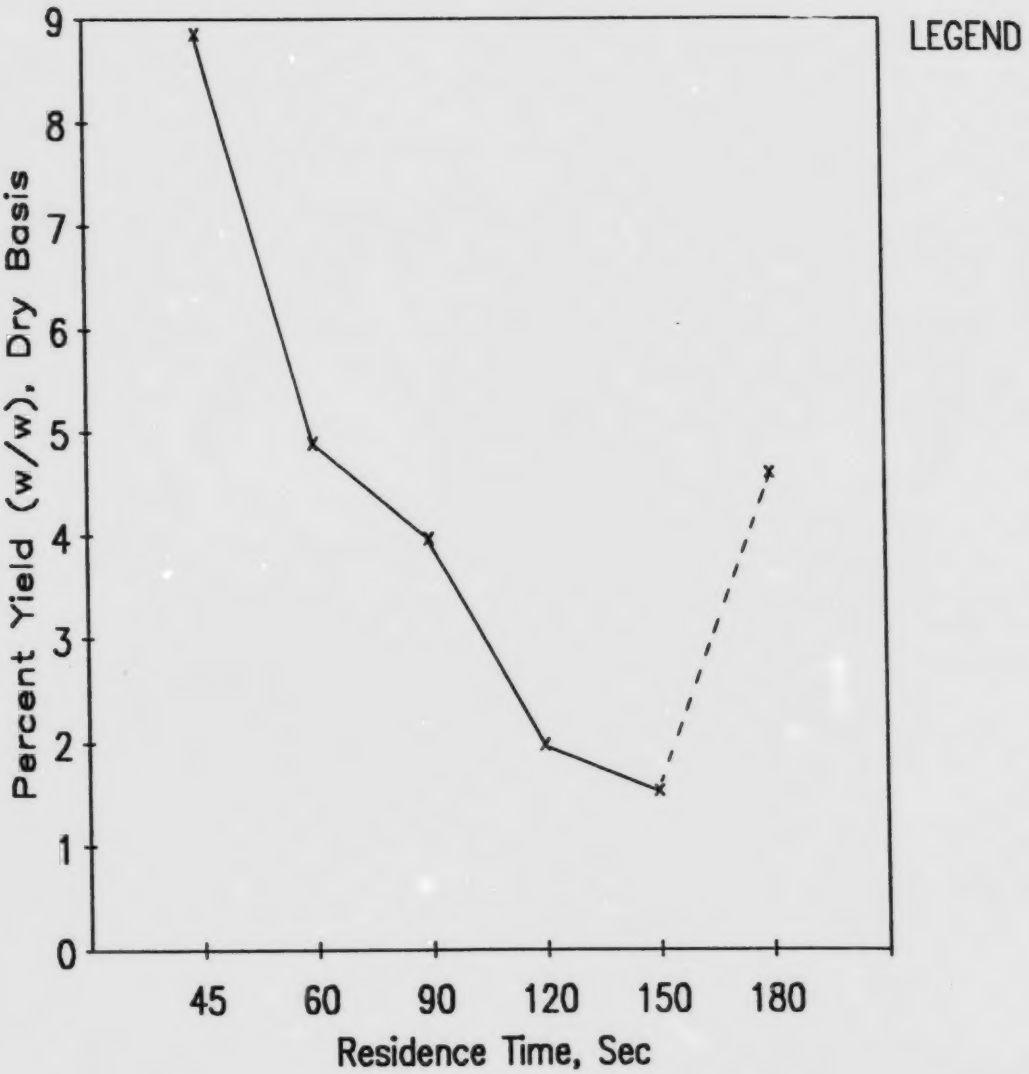
were conducted with steam at 350 ^{o}C, steam injection time of 5 sec., 1 L water in the steam generator, and approximately 100 g of IEA poplar wood chips. Reaction times of these runs varied from 45 to 180 seconds. Figure 2 shows the effect of reaction time on aqueous phase solids formation for all 17 runs. The figure adjacent to each data point is the number of runs which have been used to calculate the average yield of aqueous phase solids. The aqueous phase contains aqueous phase solids (APS) and aqueous phase organics (APO). Aqueous phase solids are partially converted lignin which remained suspended in the aqueous phase after the separation of acetone-free products. That portion of the aqueous phase solids which is soluble in acetone, is also classified as part of the oil.

It is evident from Figure 2 that the aqueous phase solids gradually decreased as the reaction time was increased. Indeed, in a separate study (Ref. 4), a relatively short reaction time (15 s) produced as high as 43 % aqueous phase solids. In the present study, at a reaction time (RT) of 150 s (two runs) the aqueous phase solids represented less than a 2 % yield. One run conducted at a RT of 180 s produced just over 4 % solids. This was not expected since a longer reaction time should result in even less aqueous phase solids. Since this material was not char this result is suspicious. It may however simply reflect variability in the feed.

The aqueous phase organics (APO) are defined as the organic products which are dissolved in the aqueous phase.

Aqueous Phase Solids Vs. Reaction Time

Steam at 350 °C, Injection Time 5 Sec.
IEA Poplar Wood Chips as Feed



Footnote: The steam generator temperature is not the sole determining factor in wood liquefaction. The reader is referred to page 23 and 25 for more information.

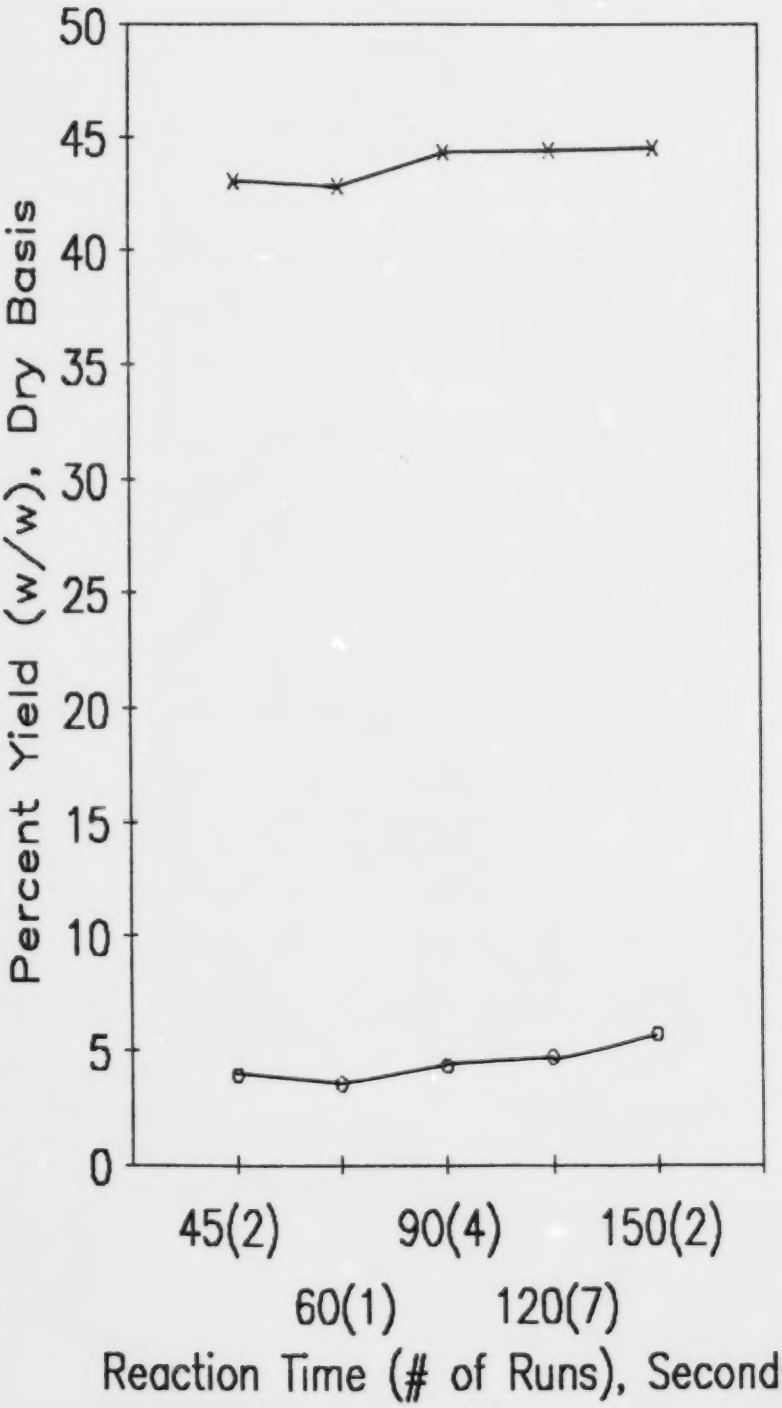
Determination of the total carbon content of the APO was required for carbon balances. Carboxylic acids in the aqueous phase were also determined (Appendix 2, page 64).

Figure 3 is constructed with 16 runs to show the effect of reaction time on oil yield. From Figure 3, it appears that the acetone-soluble as well as insoluble products (as weight % yield) increased slightly with time. However, this trend is not real. The statistical analysis of the oil yields for the seven runs made gave a mean of 44.4 % and a standard deviation of 4.7 %. The average weight percentages oil yield at a RT of 150 s (2 runs), 90 s (4 runs), 60 s (1 run), and 45 s (2 runs) were 44.5 %, 43.8 %, 42.3 %, and 43 % respectively. The average oil yield of the 16 experiments carried out at 350 ^{o}C (Figure 3) was 44.0 %, with a standard deviation of 4.2 %. The results show that the oil yield is insensitive to reaction time in the range of 45 to 150 seconds. However, the larger amount of aqueous phase solids produced at lower reaction times (Figure 2) contain acetone- soluble material (partially converted lignin) with higher molecular weights. Since this material is classified as oil, the overall quality of the oil is lowered. Reaction times of 120 s to 150 s appear to be the optimum for the liquefaction of IEA poplar wood chips in the unit, given the low amount of aqueous phase solids produced with these reaction times.

To determine the optimum steam generator temperature for wood liquefaction in the unit, six experiments were made using a

Weight Percent Yield Vs. Reaction Time

Steam at 350 °C, Injection Time of 5 Sec.



LEGEND

x Acetone–Soluble Oils

o Acetone–Insolubles

Footnote: The steam generator temperature is not the sole determining factor in wood liquefaction. The reader is referred to page 23 and 25 for more information.

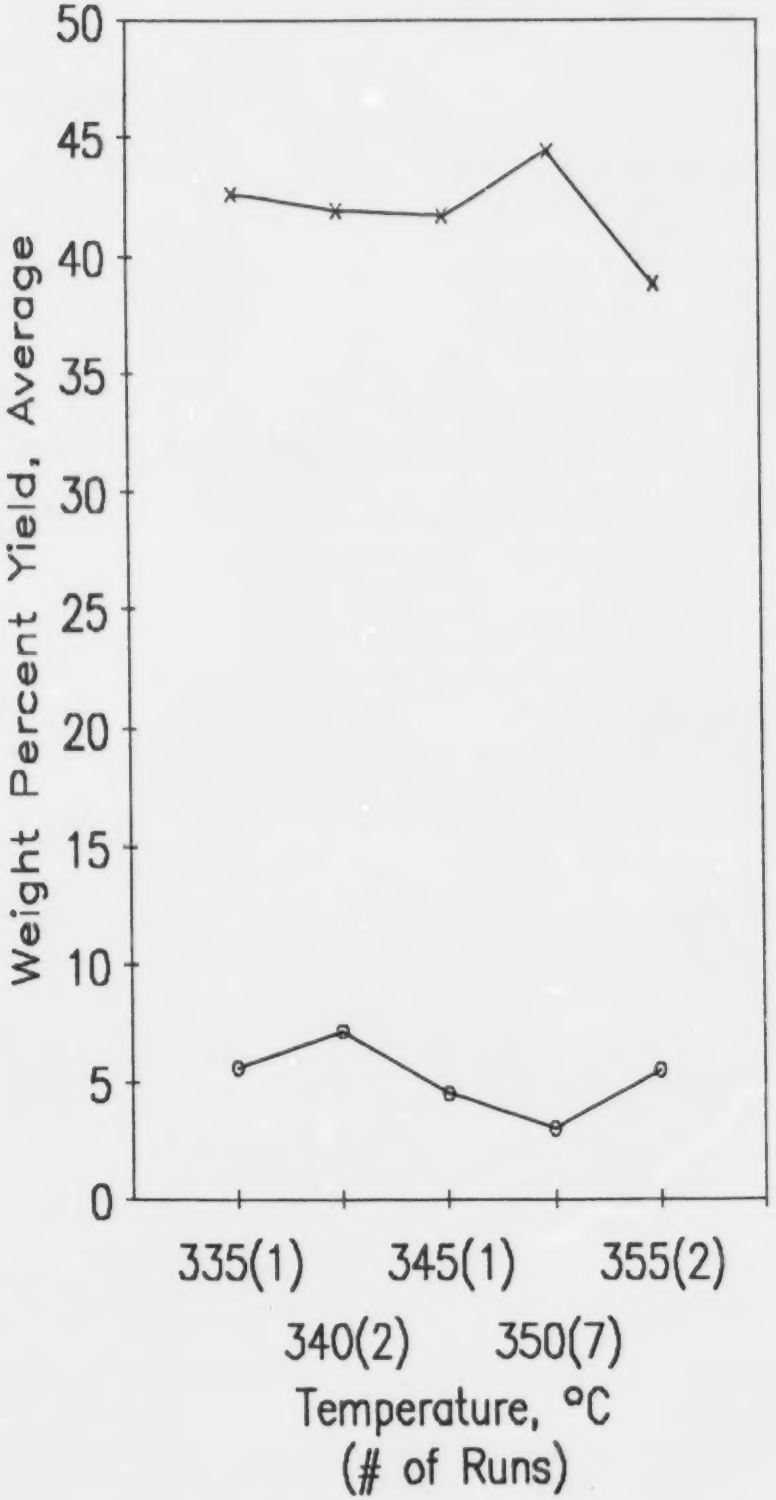
constant reaction time of 120 s and different steam temperatures. The results were combined with those from the seven runs, which used a steam temperature of 350 °C and a reaction time of 120 seconds. Figure 4 shows the weight percent yield of acetone-solubles and insolubles vs. steam temperature of these runs.

The single or average oil yield at steam temperatures of 335 °C (1 run), 340 °C (2 runs), 345 °C (1 run), and 355 °C (2 runs) were found to be 42.6 %, 41.9 %, 41.7 %, and 38.9 % respectively. The 13 runs in Figure 4, carried out at a reaction time of 120 s and at steam temperatures in the range of 335 to 355 °C, had an average oil yield of 42.8 % with a standard deviation of 4.2 %. The result shows that the oil yield again was insensitive to steam generator temperatures in the range 335 to 355 °C. However, a steam temperature of 350 °C produced less aqueous phase solids compared to other runs using different temperatures (see Figure 2). Since smaller aqueous solids content improves the quality of the oil, 350 °C appears to be the optimum steam generator temperature for the liquefaction of IEA chips in the unit.

The conditions in the reactor after steam injection will be somewhat determined by the steam generator temperature, the initial reactor temperature, and the form and mass of the substrate. Before the start of a run, the temperatures at the top and middle of the reactor are similar ($\approx$400 °C) and considerably higher than the temperature at the bottom ($\approx$ 300 °C).

Weight Percent Yield Vs. Temperature

Reaction Time of 120 Seconds



LEGEND

x Acetone–Soluble Oils

o Acetone–Insolubles

Footnote: The Steam Generator Temperature is not the Sole Determining Factor in Wood Liquefaction. The Reader is Referred to Page 23 and 25 for More Information.

When the steam enters the reactor, considerable condensation occurs which results in a water phase in the base of the reactor. The height of this water phase will depend on how much water condenses and how much void space is available. The pressure in the reactor is now controlled by the surface temperature of this water together with overpressure from product gases. However, the surface temperature of the water is not known exactly, but may presumably be calculated from the pressure in the reactor. We are planning a study of reaction conditions and their relationship to reaction severity of liquefaction as defined by Overend et al (Ref.5).

The amounts of water used (as steam) and recovered with product were relatively large compared to the feedstock. Therefore, no attempt was made to compute the complete mass balances since the results would have been of little use. On the other hand, overall carbon distribution and balances are important. Appendix 2 contains carbon distributions and balances for 12 runs. The total carbon in the products consists of the carbon in the acetone-soluble product, the aqueous phase organics, the acetone-insoluble product, and the gases. Product gas contains mostly carbon dioxide (93 %), carbon monoxide (<7 %), and traces of methane. A summary of the results of 12 runs is given in Table - 2. Ten of the 12 runs show higher (within 8.4% range of total input carbon) amounts of carbon in the total products as compared to the feed. A similar result was also reported previously (Ref. 1). The reason for this is not known but we suspect that the amount of carbon in the aqueous phase is

Table - 2 CARBON BALANCES

(Dry Basis)

RUN	Acetone-Solubles	Acetone-Insolubles	Aq. Phase Organics	Gas	Total Carbon Product	Total Carbon Wood
#	g	g	g	g	g	g
4	26.1	2.2	13.5	2.7	44.5	46.5
5	29.8	3.1	14.8	2.7	50.4	47.0
11	26.6	2.2	13.6	3.5	45.9	43.9
13	27.3	2.1	13.6	2.9	45.9	43.7
14	28.9	1.7	14.1	2.7	47.4	43.8
15	24.0	2.6	14.6	2.6	43.8	43.2
19	26.7	3.2	12.9	2.3	45.1	43.9
20	26.9	3.3	12.1*	2.9	45.2	43.9
21	24.1	9.1	8.2	2.8	44.2	44.3
23	26.2	2.7	12.4	2.8	44.1	43.5
24	26.6	1.7	13.3	3.4	45.0	44.6
25	26.6	1.9	13.6	3.1	45.2	44.2

* Carbon content calculated on the basis of another observation. Supplied value is too low compared to other runs.

lower than that actually measured.

Figure 5 depicts the percent carbon distribution in the product phases for 11 runs. Figure 5 reveals that the percent carbon in each of the product phases remains fairly constant. The distribution of product carbon with single standard deviation errors for 11 runs is 58.7 ± 0.9 % for acetone-soluble products, 29.5 ± 1.3 % for aqueous phase organics, 5.4 ± 1.3 % for acetone-insoluble products, and 6.5 ± 0.9 % for gases.

An average of 300 mL of aqueous phase was collected from the reactor when approximately 100 g of IEA wood chips were used as feed material. Usually the aqueous phase organics contained 30 % of the total carbon in the products. In two studies, attempts were made to reduce the quantity of collected aqueous phase by: (a) increasing the weight (volume) of wood fed into the reactor and thus reducing the void space , and (b) decreasing the water in the steam generator and prolonging the reaction time.

(a) In the first part of these studies, the results of two runs using larger wood dowels (3.1 cm diameter) as raw material are presented in Table - 3:

Figure 5

Percent Total Distribution of Carbon in the Products

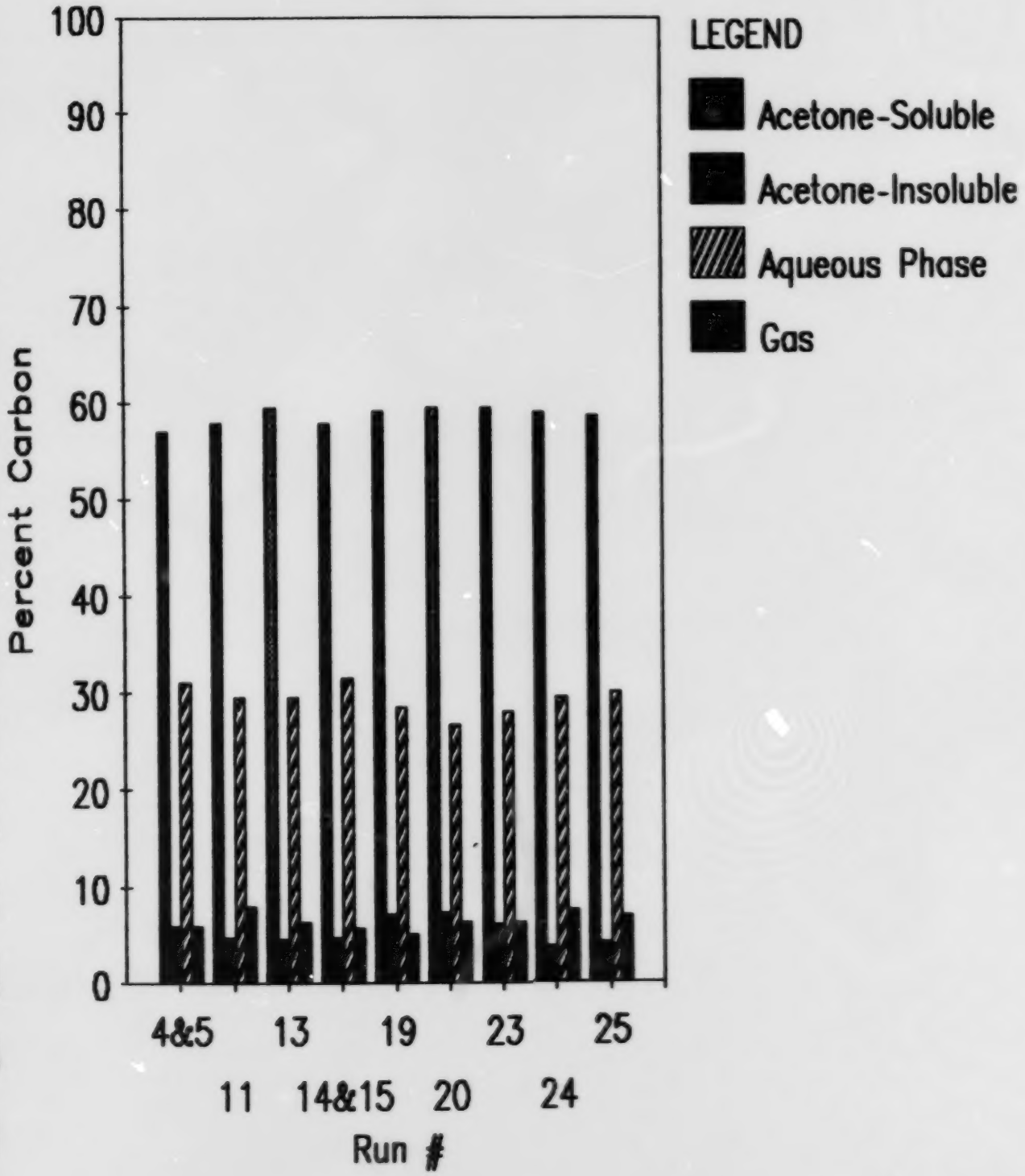


Table - 3	Run # 1	Run # 2
INPUT		
Wood Dowels (7.6 % moist.), g	161.8	167.7
Steam Temperature, ^{o}C	355.0	355.0
Steam Injection Time, sec.	5.0	5.0
Reaction Time, sec.	120.0	150.0
OUTPUT		
Acetone-solubles (dry), g	70.9	79.0
Acetone-insolubles (dry), g	13.7	6.1
Gas Volume, L	9.0	10.0
Aqueous Phase, L	340.0	290.0
Unconverted Wood, g	10.0	0.0
Wood to Aqueous Phase Ratio	1 : 2.1	1 : 1.7
Weight % Yield (dry) *	47.4	51.0
% Total Carbon Product *	68.8	73.9

* As acetone-soluble product

Since the elemental analyses for these two runs were not available, the total carbon content was calculated from data obtained in run # 25 which had similar operating conditions. These runs are significant since the ratio of wood used to aqueous phase collected increased from the usual 1 : 3 to 1 : 2. The overall yield of acetone-soluble oil also increased (50 % compared to 43.1 %). We believe, there are

significant differences in these two runs. Although the same amount of steam flashes to the reactor, there is less void space to accommodate the condensed water when the dowel diameters are larger. The water level is, therefore, initially higher in the reactor. Because the reactor wall temperature increases from bottom to top, the higher water level results in

i) higher steam pressure in the reactor (controlled by the vapour pressure of the water surface), and

ii) higher liquid heat transfer to the wood.

Thus the reactor conditions are more severe [+].

(b) In the second part of these studies, attempt was made to reduce the quantity of collected aqueous phase by decreasing the volume of water in the steam generator. Previously, either the use of steam temperatures below 335 ^{o}C or the use of less than 1 L of water in the steam generator resulted in less aqueous phase in the reactor, and an incomplete conversion at a reaction time of 120 s (Ref. 1). The effect of longer reaction times was not investigated. Therefore, two experiments were made with 0.5 L and 0.75 L of water in the steam generator, and reaction times of 150 s and 240 s respectively. The other operating conditions of the two runs were: steam temperature of 350 ^{o}C, steam injection time of 5 s, and 100 g of wood chips. It should be noted that 113 g of water are required to saturate the steam generator at 350 ^{o}C (2400 psi). Although these runs resulted in much less collected aqueous phase (150 mL and 175 mL respectively), the prolonged reaction times (150 s and 240 s) did not completely

liquefy the wood chips. The mass and heat transfer effects,as outlined in (a) above, are the main reasons for the incomplete conversion ++.

+ This aspect is covered in more detail in a subsequent report.

++ In addition to the mass and heat transfer effects as outlined in (a) above, the total heat content of the incoming steam into the reactor is also important for wood conversion. A lower water level in the steam generator resulted in a smaller quantity of steam (i.e., lower heat content) being injected into the reactor. The overall effect caused the incomplete conversion of wood.

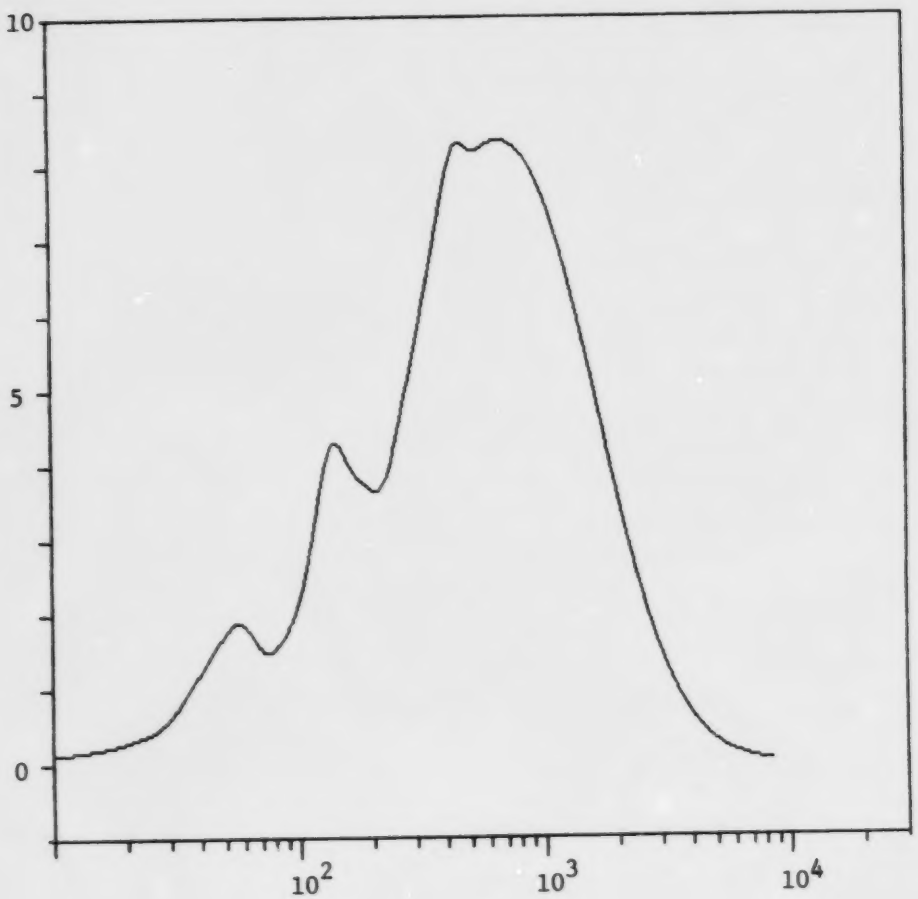
Molecular Weight Distribution of Oils

Figure 6 shows a typical apparent molecular weight distribution (polystyrene equvalent) for an acetone-free oil. High performance size exclusion chromatography (HPSEC) commonly used to determine the molecular weight distribution of synthetic polymers has been employed to compare biomass oils. HPSEC fractionates samples by molecular size in solution. The molecular weight distributions and molecular weights were calculated from the HPSEC elution profiles using the following assumptions:

1. Separation is by size exclusion only,

Figure 6

Molecular Weight Distribution of Acetone-Free Oil



Concentration (weight %)

Molecular Weight (grams/mole)

oil produced using steam at 335°C

2. Separation is complete with perfect resolution,
3. Detector response per gram is uniform across the elution profile, and
4. Molecular weight is uniquely related to molecular size in solution.

Biomass oils are a complex, heterogeneous mixture of polymers with varying chemical structures. The detector response varies as the structure of the oil changes with molecular weight. The polar nature of the compounds and their low molecular weight results in adsorption and partitioning effects in addition to separation by size exclusion. As a result, there is no unique correlation between the molecular weight of the compounds present in the oils and their retention time in the elution profile. Monodisperse polystyrene standards are used for calibration and results are expressed as polystyrene equivalent molecular weights.

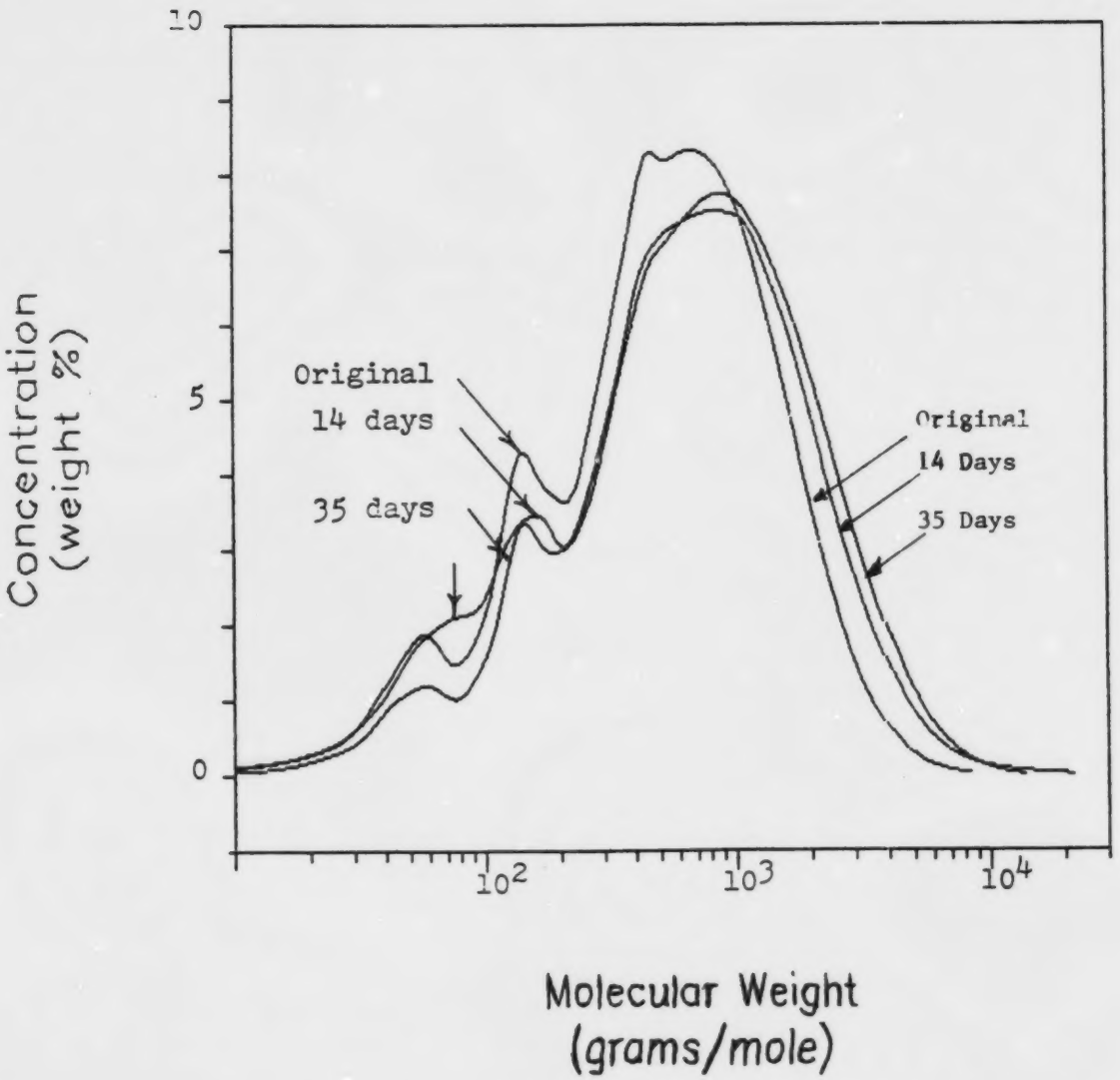
The apparent number and weight average molecular weights calculated from the distribution are 650 and 1400 respectively. Vapour pressure osmometry, the standard method for determining number average molecular weight gives a value of 675.

The oils tend to polymerize with time (Figure 7) and when heated to temperatures above 100 ^{o}C (Figure 8). Work is currently being done to improve resolution and calibration methods and identify the origin of the low molecular weight peaks.

Figure 7

Variations in the Molecular Weight Distribution of Acetone-Free Oil With Time

(stored in THF)

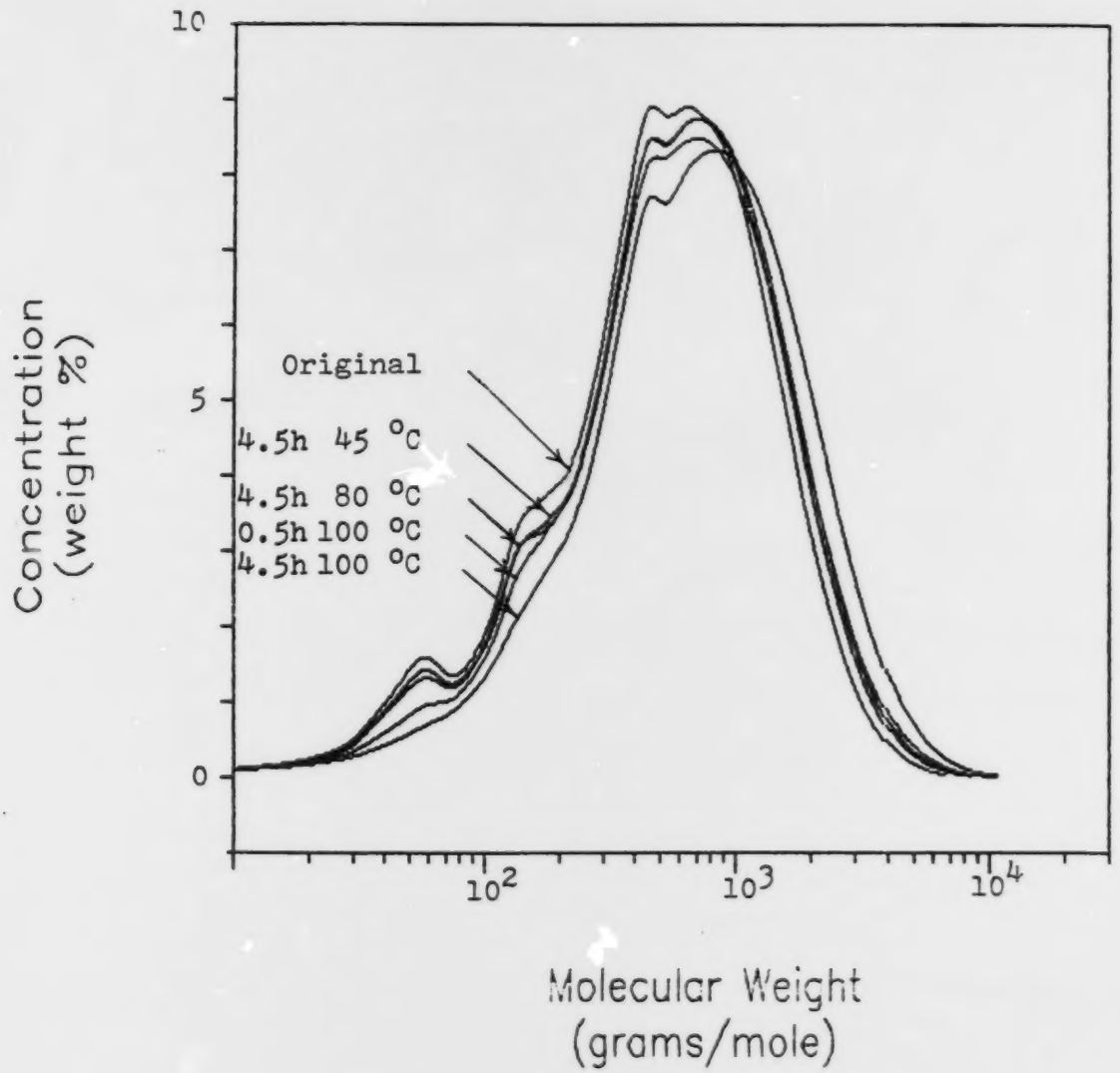


oil produced using steam at 355°(

Figure 8

Variations in the Molecular Weight Distribution of Acetone-Free Oil With Heating

(heated in open containers)



oil produced using steam at 355 °C

The Proton and Carbon-13 NMR Analysis

Proton and carbon-13 Nuclear Magnetic Resonance (NMR) were used to identify the nature of the aqueous phase organics and the acetone-soluble products. Figure 9 shows the proton spectrum of acetone-free oil. It clearly shows methoxyl protons at around 4 ppm and aromatic protons at 7 - 8 ppm. The signal at 4.8 ppm is due to hydroxyl protons and as is usual, shifts in other spectra due to changes in solution concentration. Figures 10, 11, and 12 are all decoupled carbon-13 spectra of the acetone-free oil. Carbon-13 atoms only have a natural abundance of 1 % and therefore multiple scans must be made and the signals added. Figure 10 is the result of 3200 scans with a delay of 0.5 second between successive scans. This delay time is too short for complete relaxation of the carbon-13 nuclei, and the resulting peak areas and intensities cannot be used for any kind of relative quantitation of carbon atoms. It does, however, give a relatively fast qualitative picture of the sample. The methoxyl carbons are clearly evident at 58 ppm. Figure 11 is the result of 25,000 scans in which the signal to noise ratio is significantly increased. Figure 12 is the result of 6000 scans with a 6 seconds delay time. In this case signal areas can be used to estimate the content of some types of carbon atoms in the sample.

Figure 13 is the proton NMR spectrum of the aqueous phase and shows no useful information. Figures 14, 15 and 16 show the

Figure 9

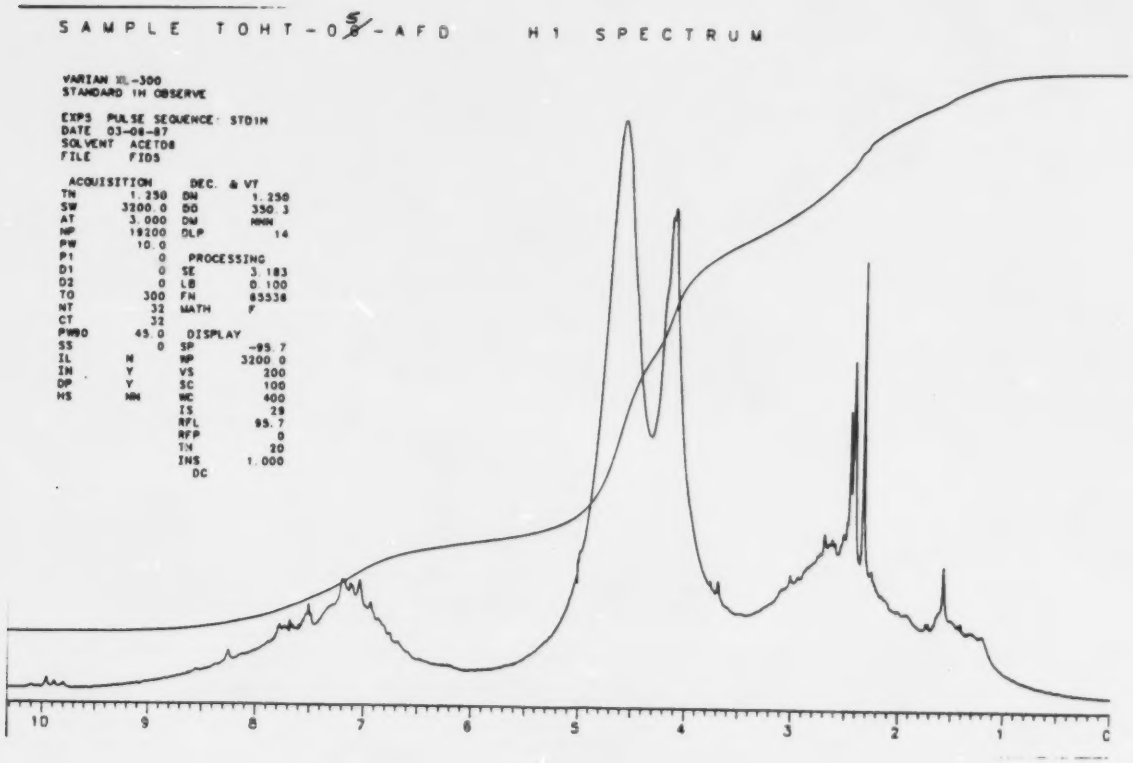


Figure 10

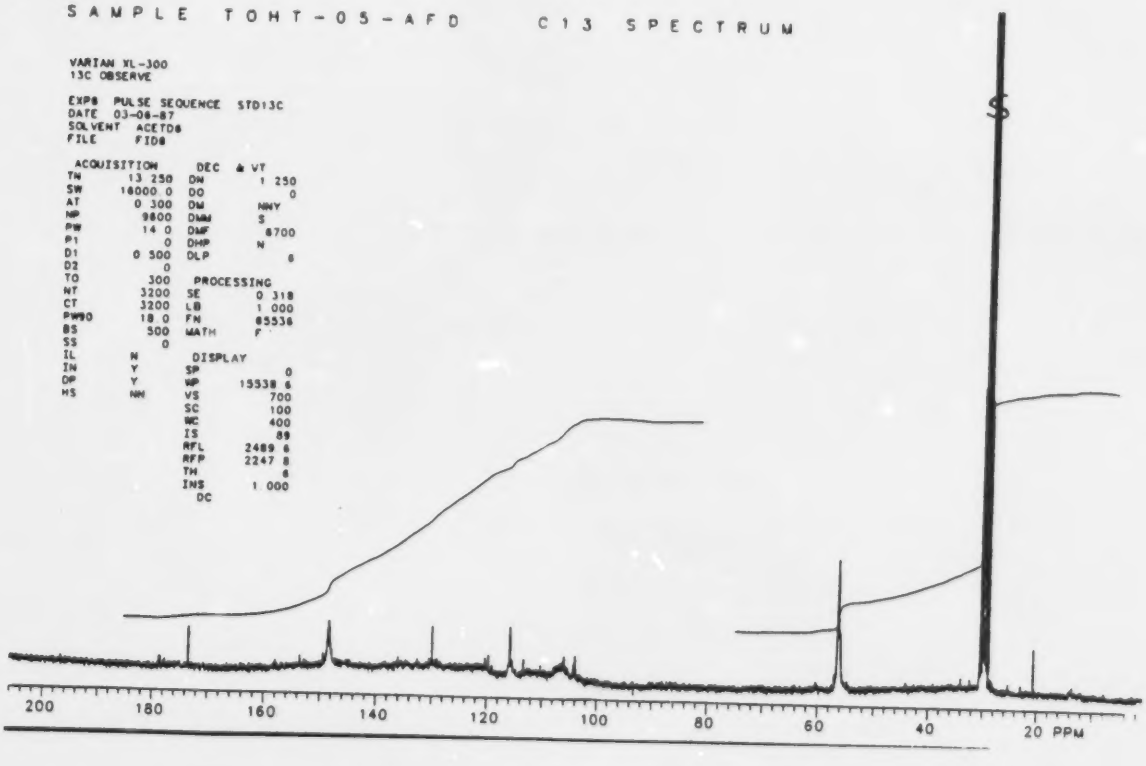


Figure 11

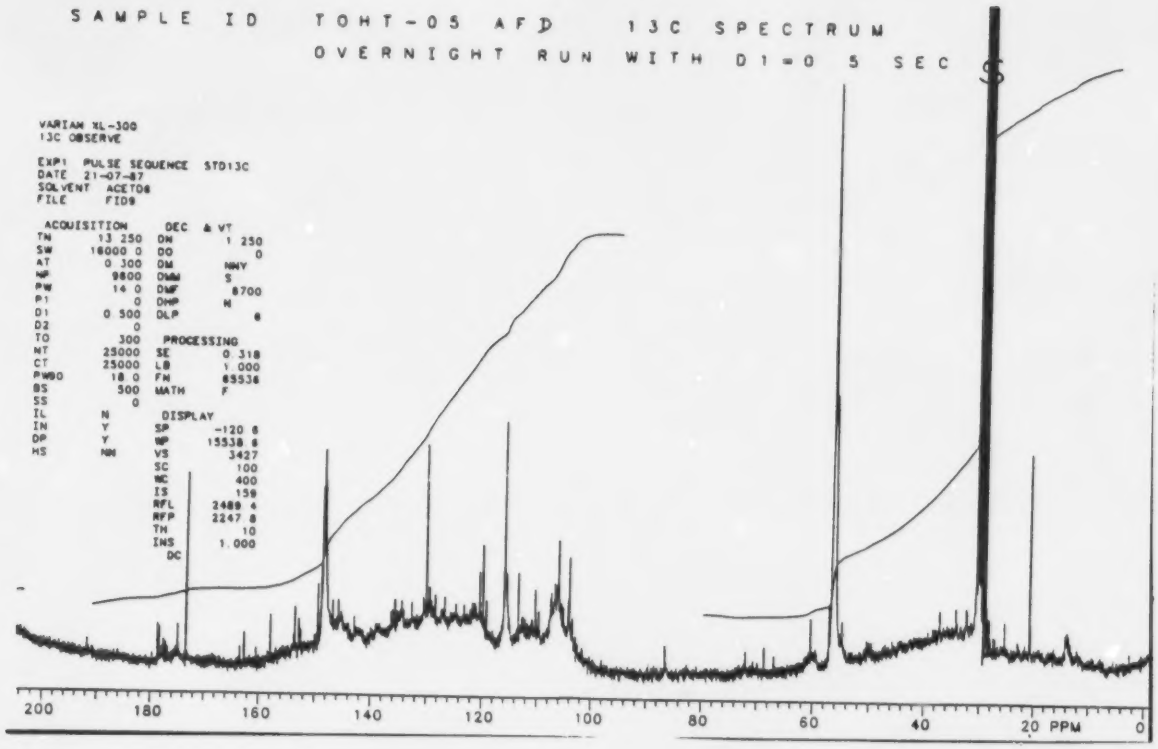


Figure 12

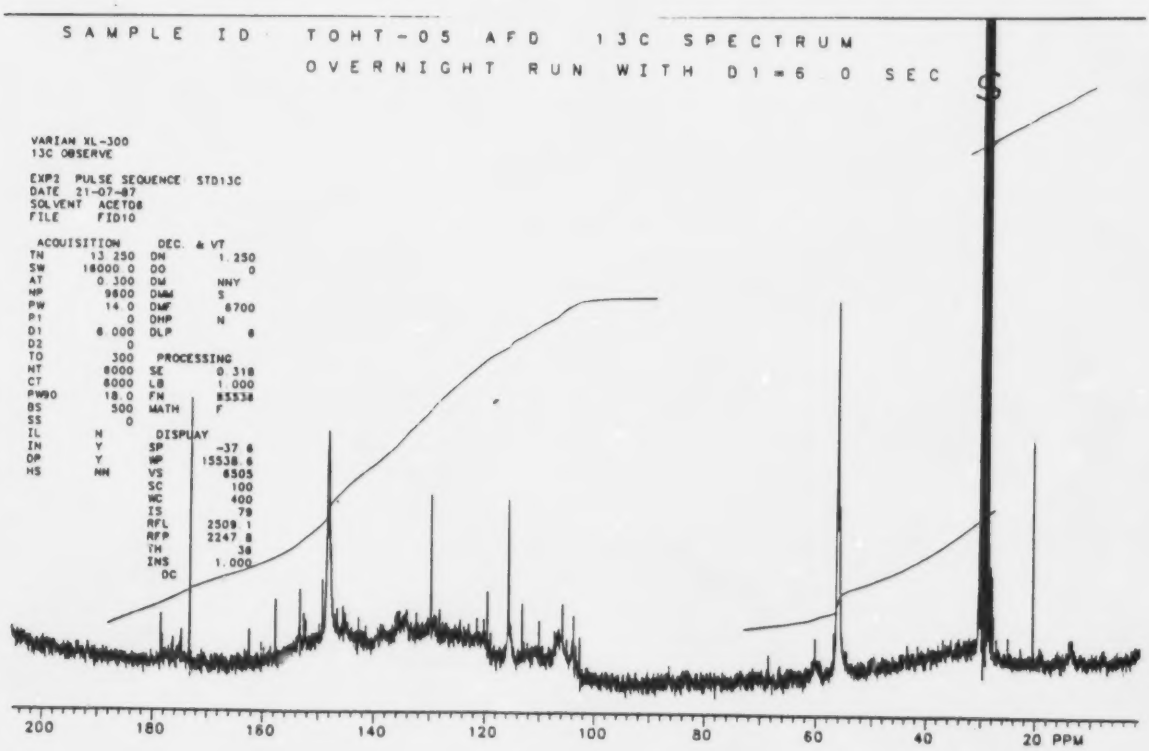


Figure 13

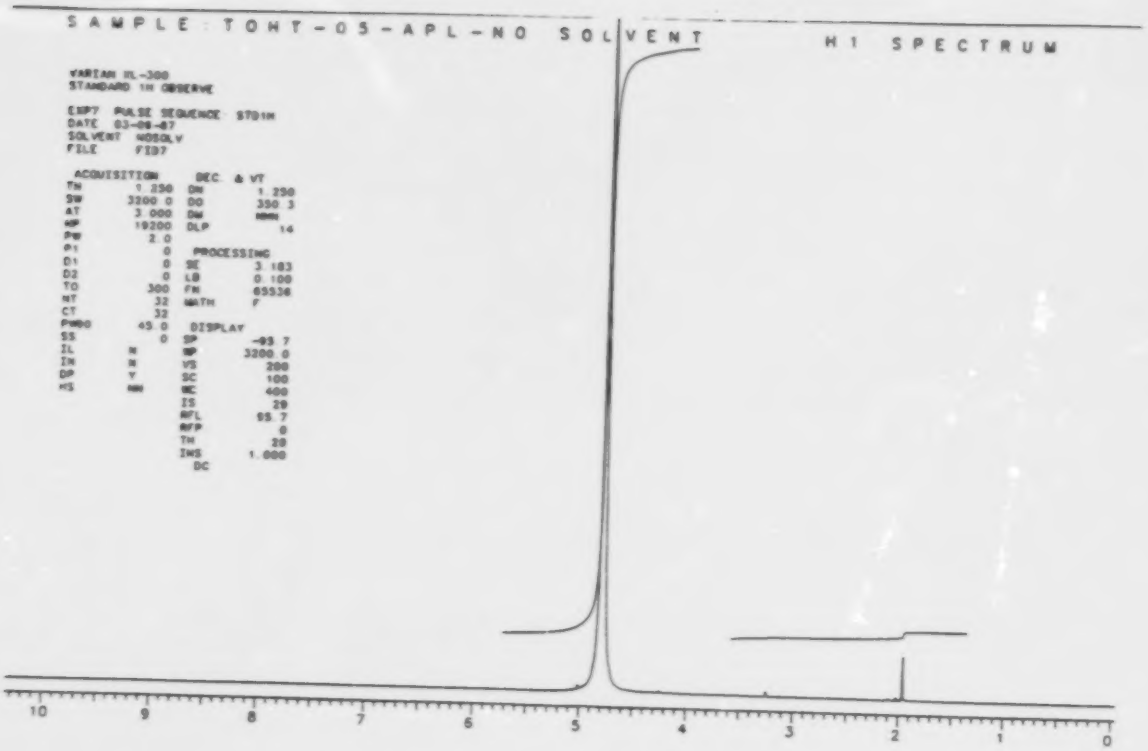


Figure 14

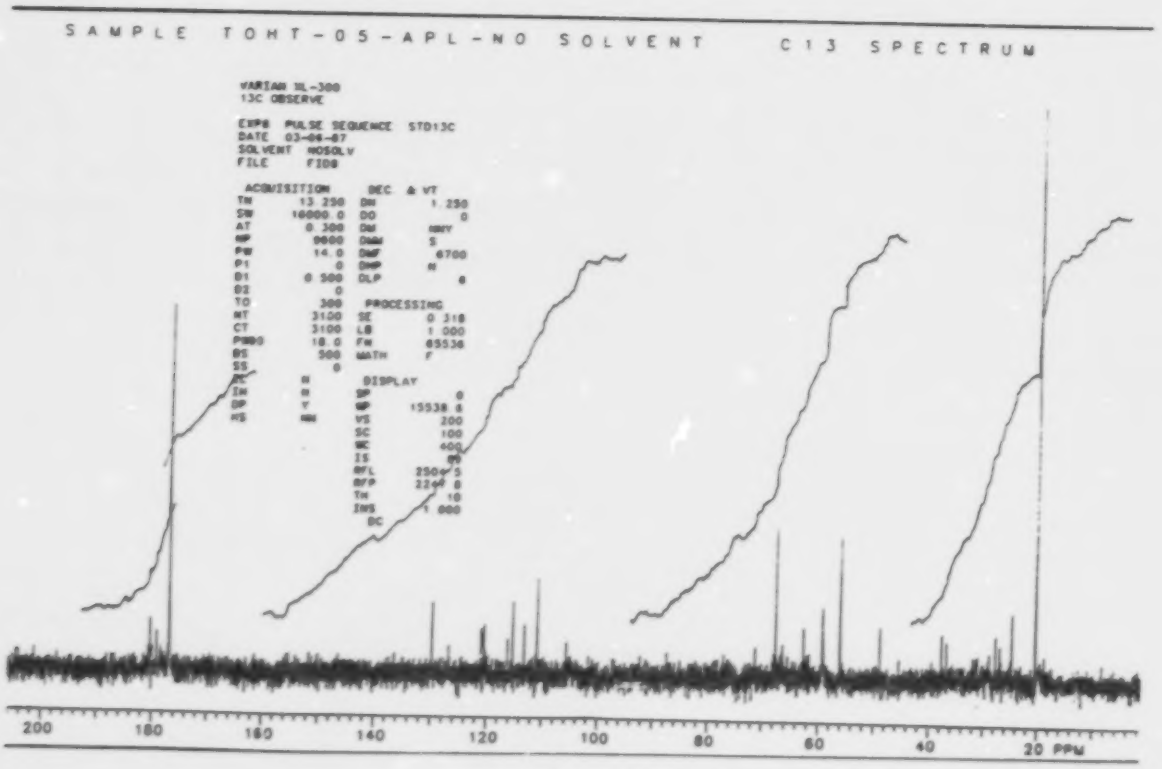


Figure 15

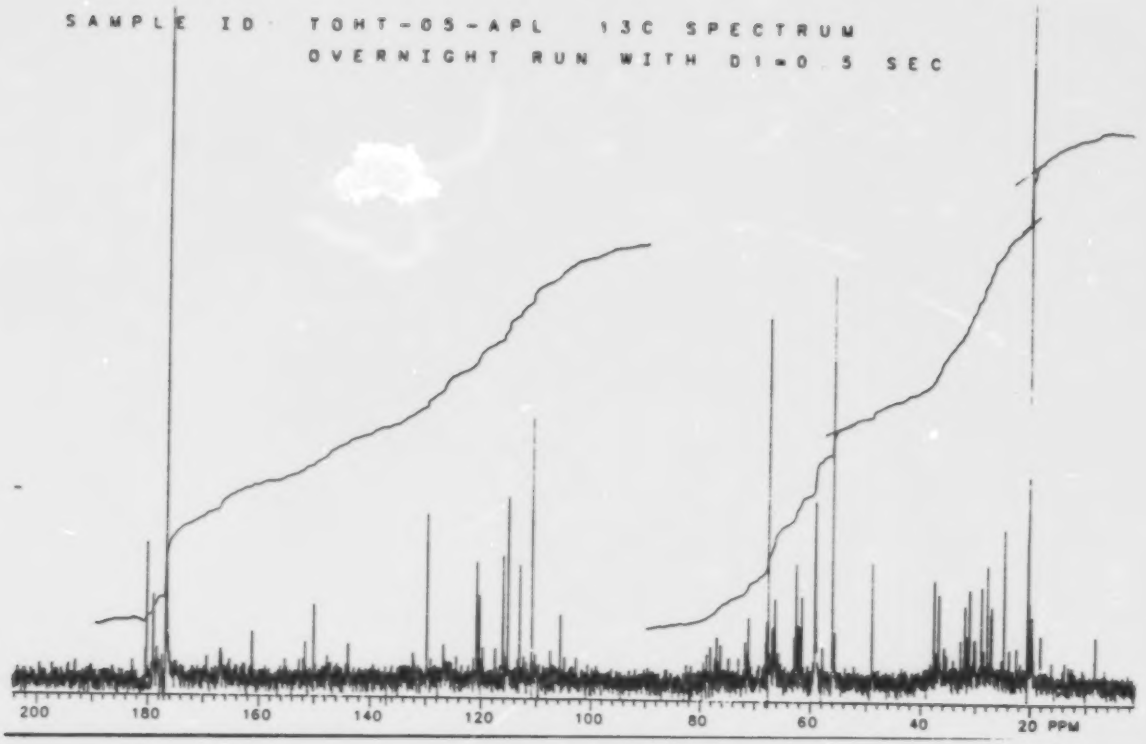
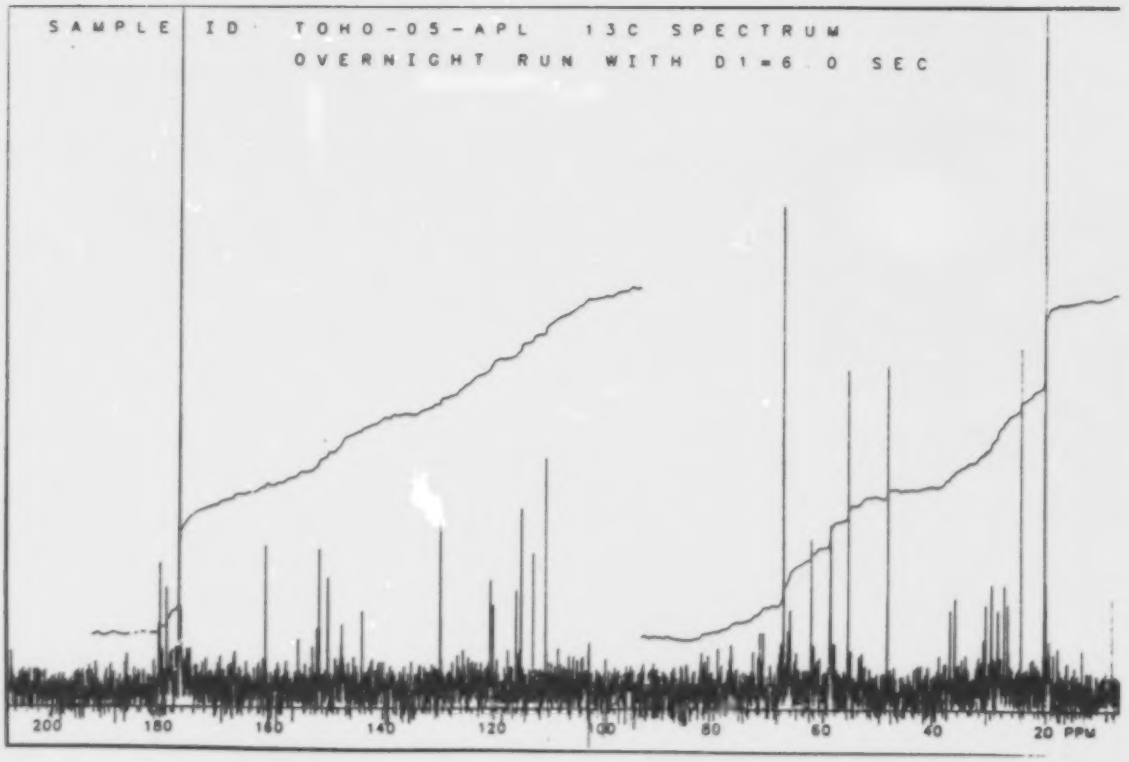


Figure 16



carbon-13 spectra of the aqueous phase run under essentially the same conditions as spectra shown in Figures 10, 11 and 12. Thus, spectrum 15 is the most intense and spectrum 16 can be used for approximate concentrations. Clearly the most abundant component is acetic acid with the methyl carbon at 20 ppm and the carboxyl carbon at 177 ppm. The methoxyl signal is also present (56 ppm).

One major difference which has been noticed between fast pyrolysis oils, such as those produced at the University of Waterloo, and our oils is the degree of sharpness in the proton and carbon-13 spectra. The Toronto spectra are broader, and initially it was thought that the presence of paramagnetic ions (from the reactor) was the cause. Therefore, spectra (Figures 17 and 18) of a second Toronto oil were compared to those of a University of Waterloo oil (Figures 19 and 20). In addition, a mixed sample was run (Figures 21 and 22). If paramagnetic ions were broadening the spectra of the Toronto oils then the mixed sample should also show broadening. This was not the case, and it shows that the broad spectra of the Toronto samples are real. The acetic acid which is in the aqueous phase from the Toronto process is in the 'oil' from the Waterloo process. However, the Waterloo product also contains considerable water. It is concluded that some products that appear in the fast pyrolysis oils are tranferred to the aqueous phase in the Toronto process.

Figure 17

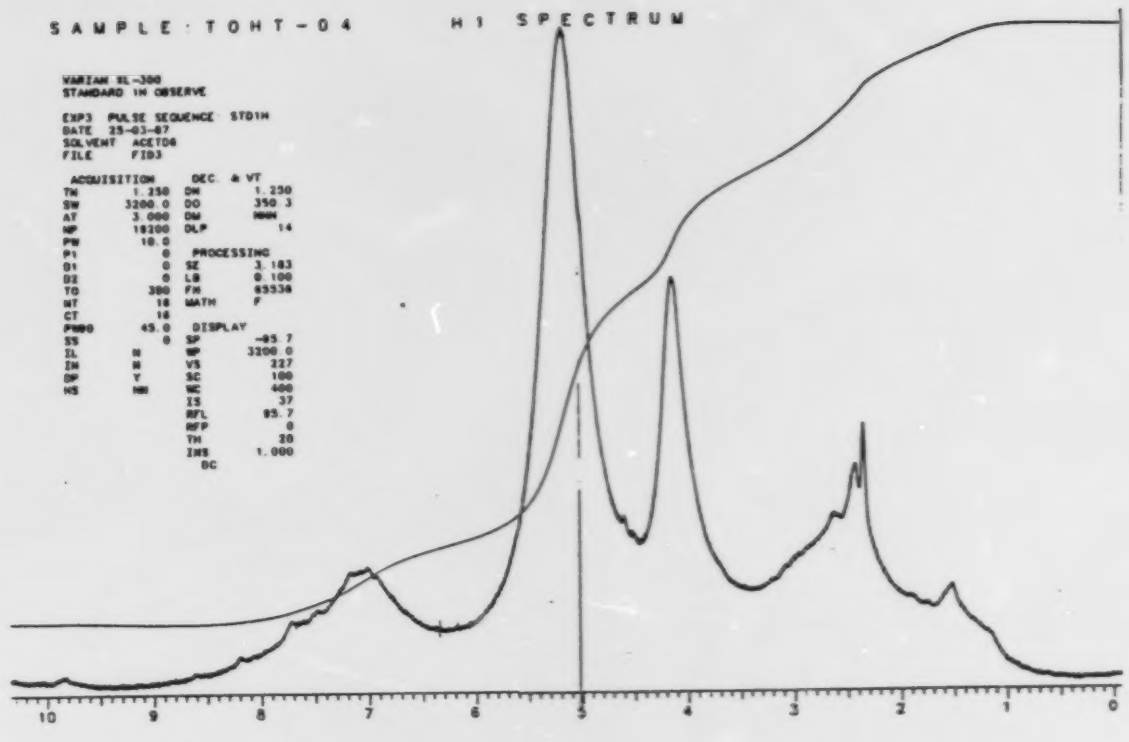


Figure 18

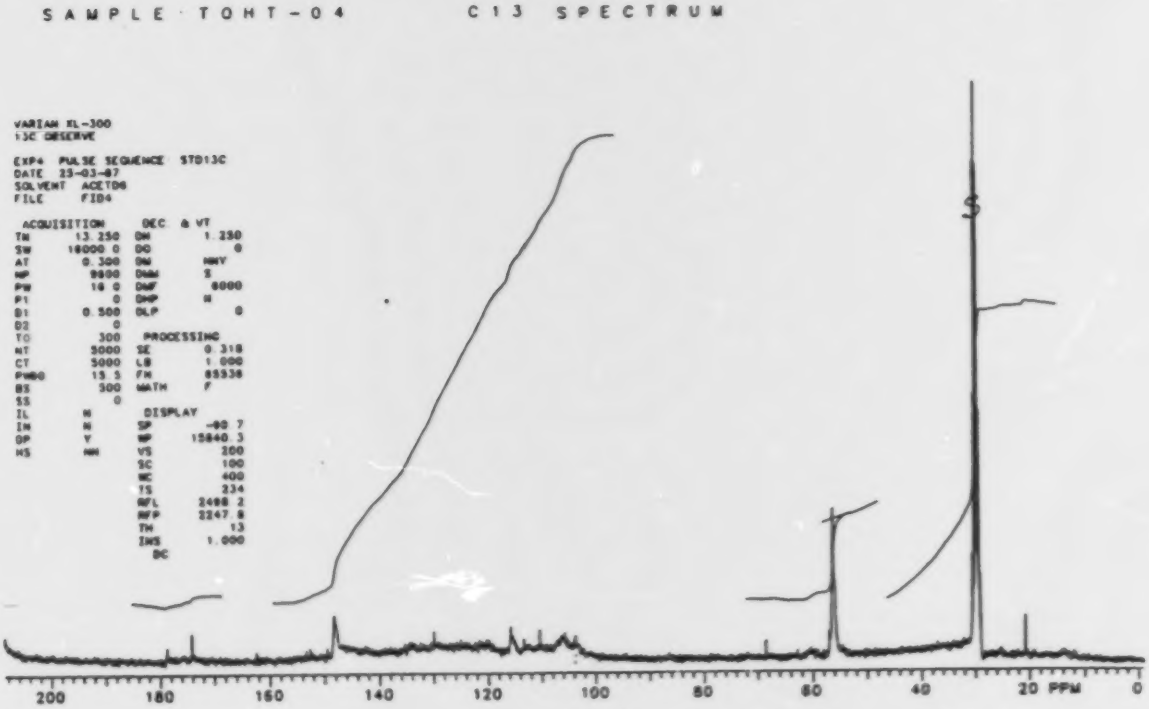


Figure 19

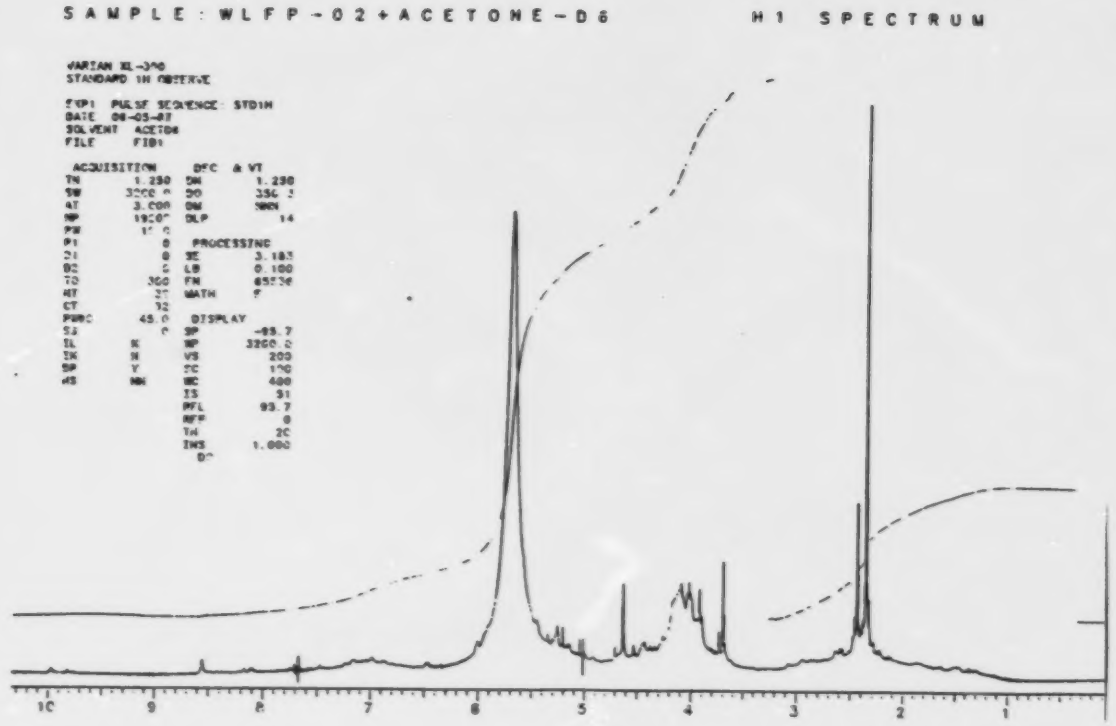


Figure 20

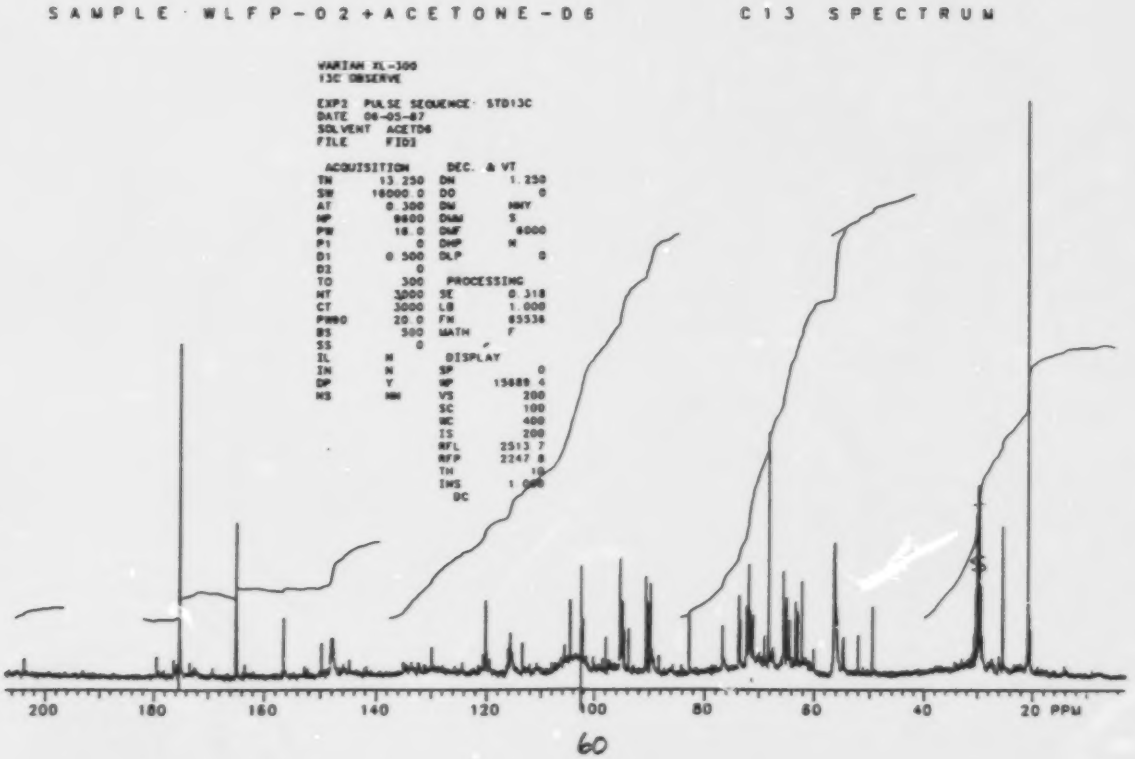


Figure 21

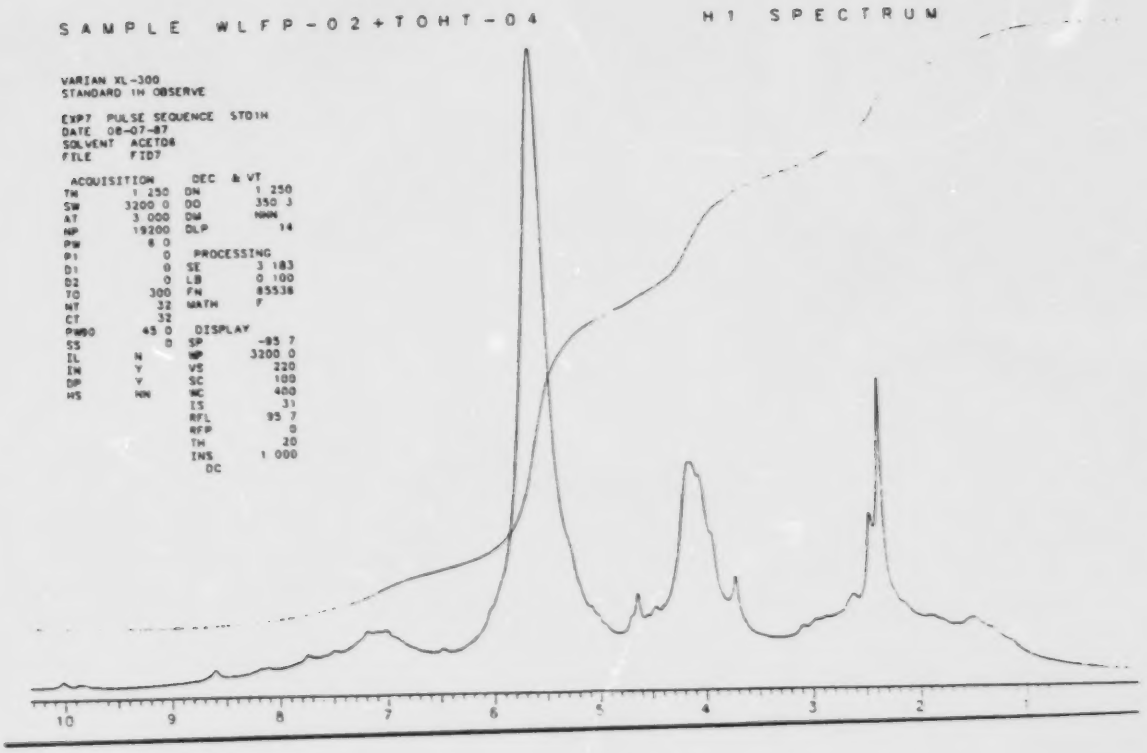
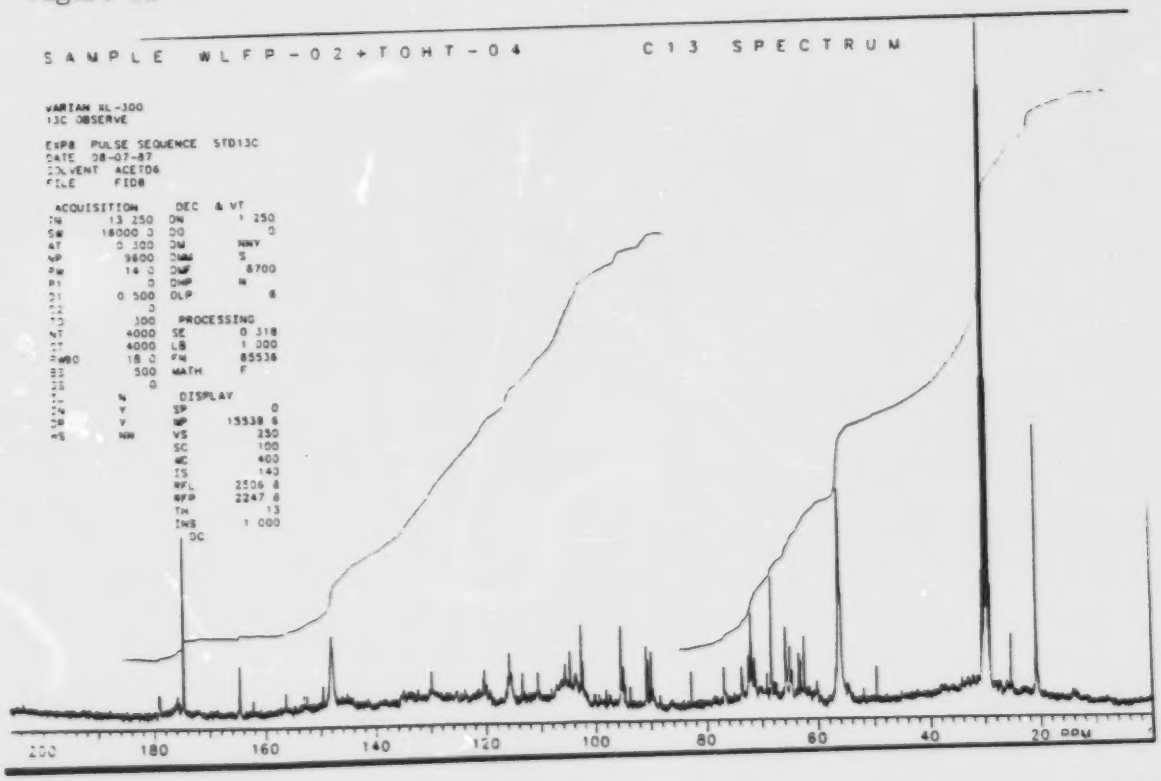


Figure 22



3.1 CONCLUSION

(a) IEA poplar wood chips were used to produce acetone-soluble oils, aqueous phase organics, acetone-insolubles, and gases using steam in the temperature range 335 to 355 ^{o}C and the reaction time in the range 45 to 150 seconds.

(b) Very similar oil yields (43.1 %, w/w) were obtained within the steam temperature and reaction time ranges as in (a).

(c) The collected aqueous phase to wood ratio for a run using approximately 100 g of wood chips as feed material was found to be 3 : 1. This ratio diminished to 2 : 1 when 160 g of wood dowels were used. Higher oil yield (50 %, w/w) was also observed in the case of lower collected aqueous phase to wood ratio. Further investigation is underway to verify these results.

(d) Runs with lower steam temperatures (335 ^{o}C and below) and reaction times (e.g., 45 s and below) produced more aqueous phase solids, which were partly acetone-soluble.

(e) The average weight percent yield of oil from IEA wood chips is 43.1 % which represents 58.7 % of the total carbon in the product. The remaining product phases, namely acetone-insolubles, aqueous phase organics, and gases, represent 5.4 %, 29.5 %, and 6.4 % respectively of the total carbon in the product.

(f) Wood chips were not converted completely with prolonged reaction time (4 minutes) when less than 1 L of water was present in the 2 L steam generator. This is an observation

which is related to the relative sizes of the steam generator and the reactor, and the temperature in the latter.

(g) On the basis of aqueous phase solid content of the oil products, which determines the oil quality, the optimum steam temperature and reaction time for the IEA wood chips liquefaction in this unit appear to be 350 ^{o}C and 120 s or 150 s respectively.

(h) The apparent number and weight average molecular weights of oil were found to be 600 and 1400 respectively. With time, the oil slowly polymerized, but the average molecular weight did not increase dramatically. The oil repolymerized rapidly when heated to 100 ^{o}C.

(i) Carbon-13 nuclear magnetic resonance revealed that there were numerous organic compounds present in the aqueous phase. The predominant compound was acetic acid. The aromatic methoxyl signal was also strong. Analysis of a co-mixture of oils from the University of Toronto and Waterloo illustrates that the broad carbon-13 spectra of the U of T oil samples are real, and are not due to the presence of paramagnetic ions.

3.2 RECOMMENDATIONS

It is recommended that:

(a) More studies, using higher volume wood dowels as feed material should be continued to investigate the apparent higher oil yields resulting from less reactor void space.

(b) The system should be upgraded by further insulating the reactor top and bottom valves and their operators so as to reduce the heat loss during operation, and in particular, reduce the volume of condensed water in the reactor. It is important that the initial temperature throughout the reactor be higher than the injected steam temperature.

(c) The recently procured pressure transducer should be fully utilized during future runs.

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3.4 The Product Nomenclature

The following definitions should help the reader identify the various products mentioned in the text:

Oil or Acetone-Soluble Product (ASP): Non-gaseous product which phase separates from water and is soluble in acetone. This is usually made up of three fractions:

a) The acetone-soluble portion of the acetone-free product (AFP)
b) Acetone-wash product (AWP), and
c) The acetone-soluble aqueous phase solids.
(see following definitions)

Acetone-free Product (AFP): That portion of the product which is recovered directly by phase separation from the water. It is solid (black) at room temperature and contains mostly acetone-soluble material.

Acetone-wash Product (AWP): That portion of the product recovered by washing the reactor, feed basket, let-down lock, and product receiver with acetone, followed by filtration

of the wash liquid and removal of the acetone by rotary evaporation.

Aqueous Phase (AP): This term refers to the aqueous phase product which usually contains dissolved organics and sometimes suspended materials which are called aqueous phase solids (APS).

Acetone-soluble portion of the aqueous phase solids (APS): This is self-explanatory, being that portion of the suspended material in the "product" aqueous phase, which after separation by centrifugation, is soluble in acetone.

Aqueous phase organics (APO): The organic products which are dissolved in the aqueous phase.

Acetone-insolubles (AI) (char and unconverted material not soluble in acetone): This is a composite fraction made up of:

a) Acetone-insoluble material from the acetone-free product (AFP),
b) Material recovered from the feed basket after acetone-washing and filtration of AWP, and
c) The acetone-insoluble fraction

of the aqueous phase suspended solids.

Gases: Gases produced from the reaction.

IEA: IEA stands for International Energy Agency. Countries involved in an IEA agreement on thermal liquefaction of biomass include: Canada, USA, Finland and Sweden.

D38: It refers to the clone type of the particular wood (in this case poplar deltoides) under investigation.

TOC: Total carbon in the aqueous phase organics.

4.1 APPENDIX 1

TABLE - 1 OPERATING CONDITIONS OF RUN

RUN #	WOOD CHIPS (Dry) g	STEAM TEMP. (^{O}C)	STEAM INJECT. TIME (SEC)	REACTION TIME (SEC)	REACTOR TEMPERATURE T2-T4-T5 (^{O}C)
1	88.9	350	5	90	280-408-415
2	84.2	350	5	120	290-416-406
3	95.4	350	5	150	291-409-412
4	98.3	350	5	120	291-424-419
5	99.4	350	5	120	290-408-408
6	93.9	350	5	90	300-421-414
7	95.6	350	5	180	299-418-395
8	92.3	350	5	150	300-403-397
9	91.5	350	5	120	301-404-409
10	95.4	350	5	120	300-395-398
11	92.8	350	5	90	300-407-404
12	91.7	350	5	90	300-409-409
13	92.4	350	5	60	300-405-410
14	92.6	350	5	45	301-405-409
15	91.4	350	5	45	301-407-410
16	92.2	350	3	120	307-409-412
17	92.0	350	2	120	300-417-418
18	91.4	355	2	120	306-415-425
19	92.9	340	5	120	306-422-425
20	92.8	340	3	150	306-401-421
21	93.7	340	3	120	300-414-413
22	92.2	340	3	180	308-432-431
23	92.0	335	5	120	307-425-432
24	94.3	345	5	120	308-427-432
25	93.5	355	3	120	309-413-422

TABLE - 2

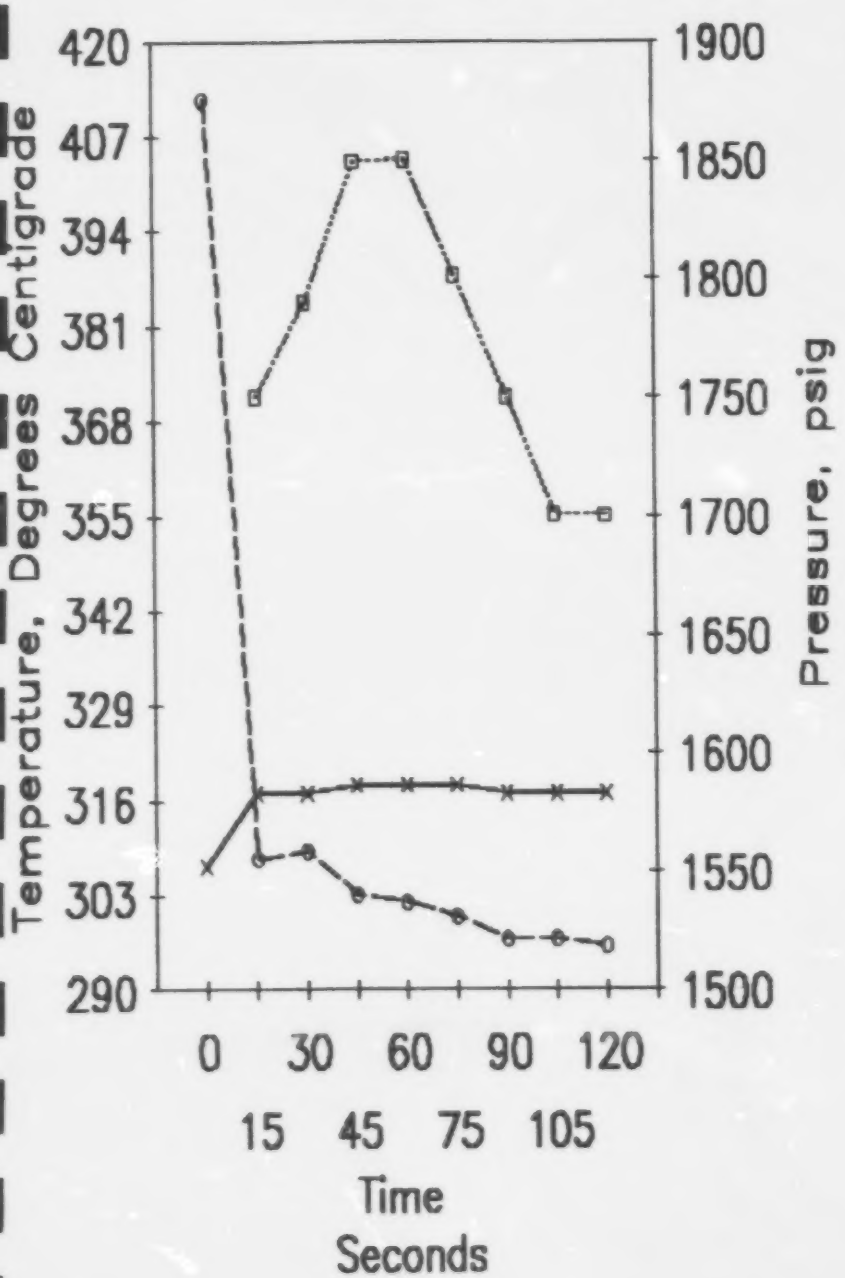
PRODUCTS
(Dry Basis)

RUN #	AFP (*) g	AWP (*) g	APS (*) g	CHAR (*) g	AP (*) mL	ACETONE-SOLUBLES g	ACETONE-INSOLUBLES g
1	18.1	15.6	6.6	2.1	300	36.8	5.6
2	20.2	17.2	7.7	4.5	290	43.7	6.0
3	20.8	19.7	1.8	4.4	295	41.7	4.8
4	30.6	7.3	0.9	2.6	310	38.1	3.3
5	20.6	16.5	8.1	3.6	290	44.0	4.8
6	28.3	13.4	8.1	3.0	300	48.5	4.4
7	18.8	26.0	4.4	4.9	350	48.7	5.5
8	25.2	16.5	1.1	4.7	325	41.8	5.7
9	23.9	20.6	1.2	2.9	300	45.6	3.0
10	12.1	28.9	0.1	3.0	330	41.0	3.0
11	7.0	31.3	0.1	3.2	300	38.3	3.4
12	17.6	18.9	2.8	2.3	325	39.1	2.6
13	19.6	16.5	3.7	2.0	300	39.5	3.2
14	23.1	13.2	7.1	1.6	305	43.4	2.9
15	17.6	12.1	6.5	2.5	355	36.2	4.3
16	20.7	18.2	0.9	2.7	265	39.4	3.3
17	27.2	10.8	0.4	5.8	290	36.6	7.7
18	12.3	16.7	8.3	3.8	325	32.6	8.4
19	20.1	16.9	3.7	3.6	300	39.6	4.7
20	17.6	19.0	7.1	4.1	290	39.9	4.9
21	19.3	14.4	9.8	1.4	255	38.5	16.3
22	27.3	9.7	3.8	3.5	285	38.9	5.3
23	22.4	12.4	5.2	3.2	305	39.1	4.1
24	23.2	12.3	4.2	2.2	310	39.4	2.6
25	22.4	15.7	1.8	2.2	325	39.1	2.9

(*) Definitions of these terms are given in the nomenclature.

Temperature, Pressure Profiles

Steam for 7 Seconds
350 C, 2400 psig
1.0 L Water in SG



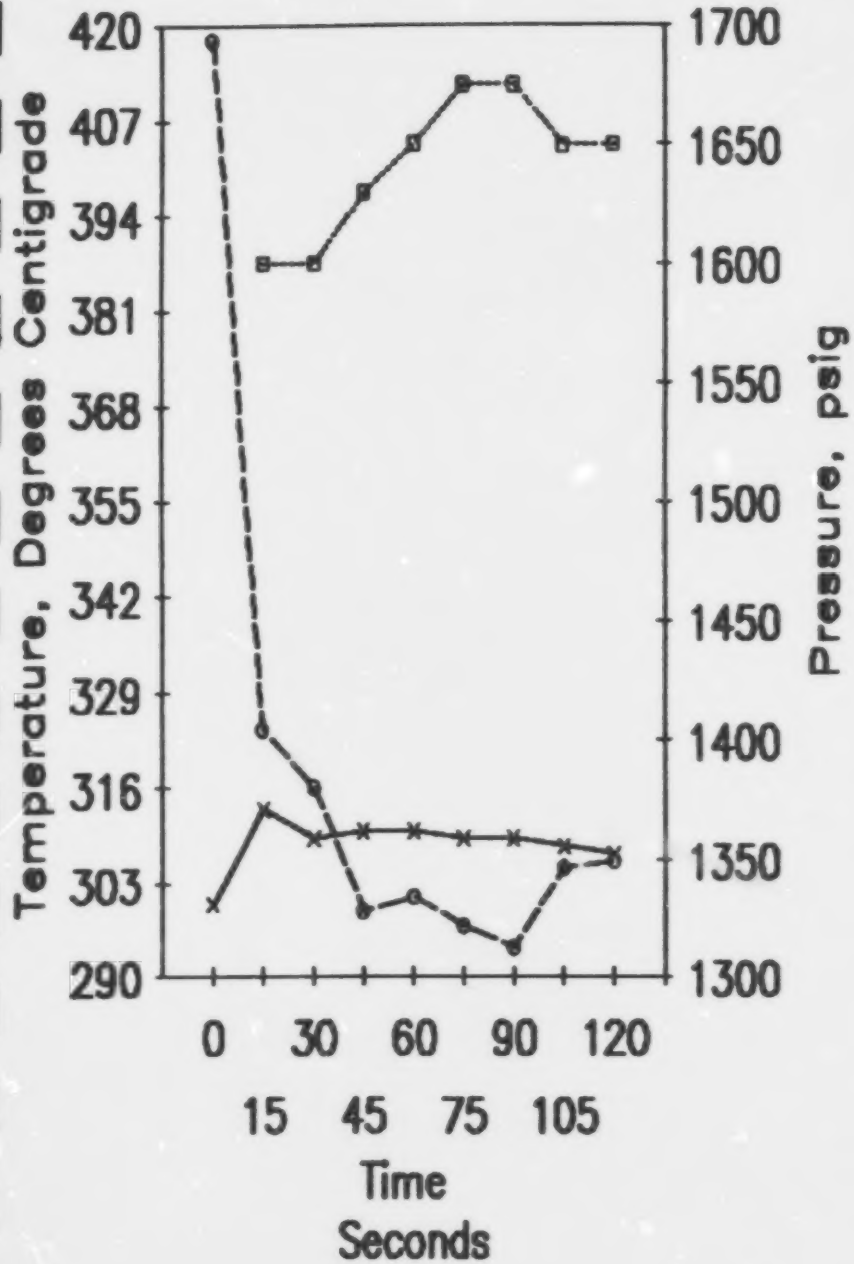
LEGEND

- x T2 bottom of CR
- o T5 top of CR
- □ CR pressure

RUN # 16, IEA Poplar Wood Chips

Temperature, Pressure Profiles

Steam for 2 Seconds
350°C, 2400 psig
1.0 L Water in SG



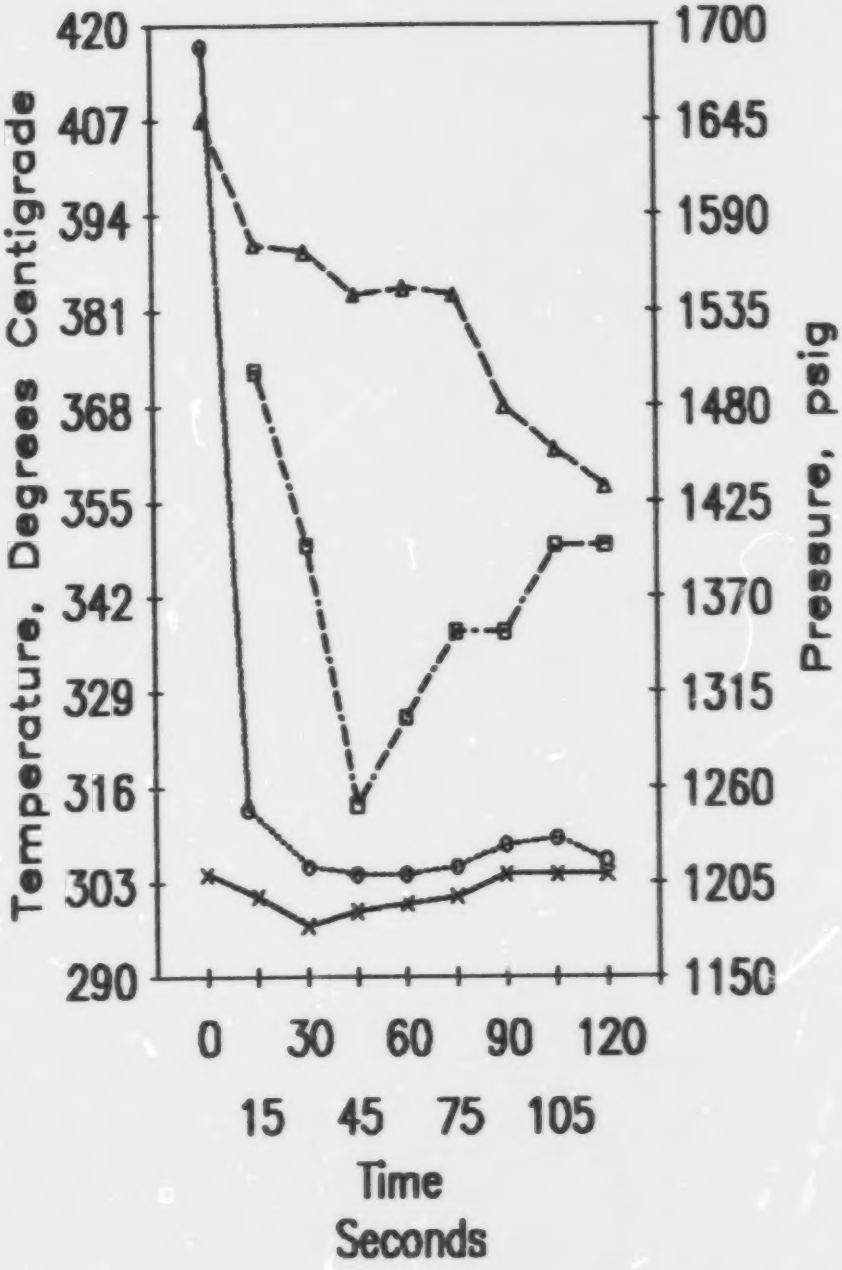
LEGEND

- x T2 bottom of CR
- o T5 top of CR
- □ CR pressure

RUN # 17, IEA Poplar Wood Chips

Temperature, Pressure Profiles

Steam for 2 Seconds
355°C, 2600 psig
1.0 L Water in SG



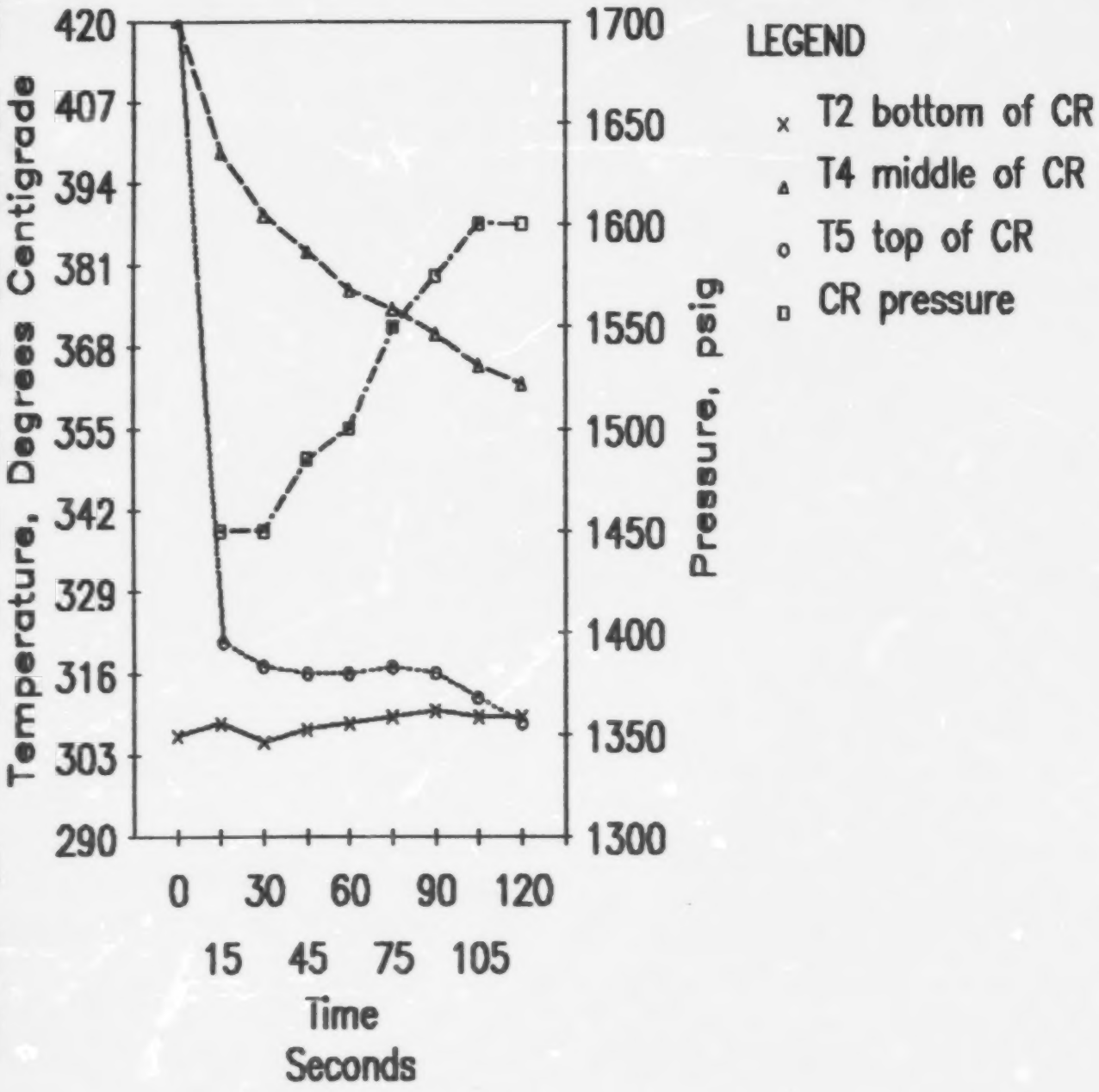
LEGEND

- x T2 bottom of CR
- △ T4 middle of CR
- o T5 top of CR
- □ CR pressure

RUN # 18, IEA Poplar Wood Chips

Temperature, Pressure Profiles

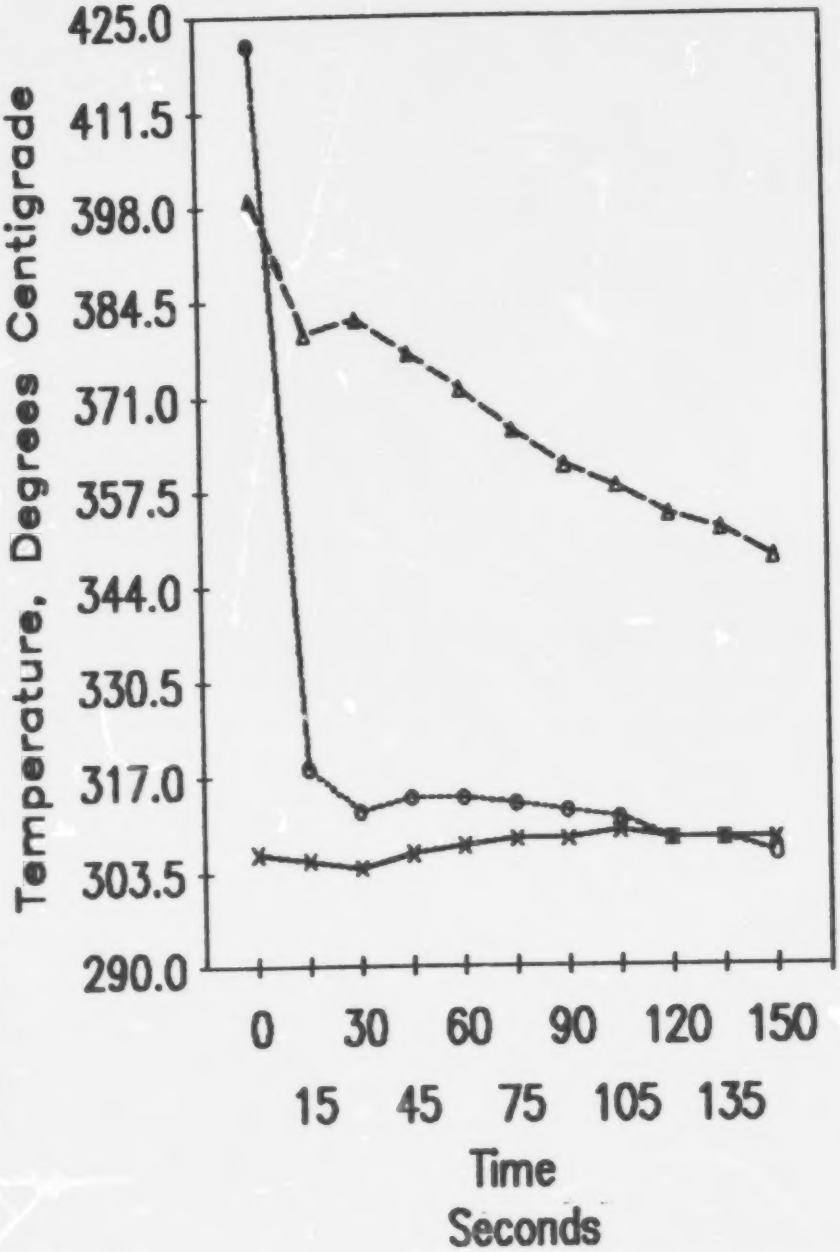
Steam for 5 Seconds
340°C, 2100 psig
1.0 L Water in SG



RUN # 19, IEA POPLAR WOOD CHIPS

Temperature Profiles

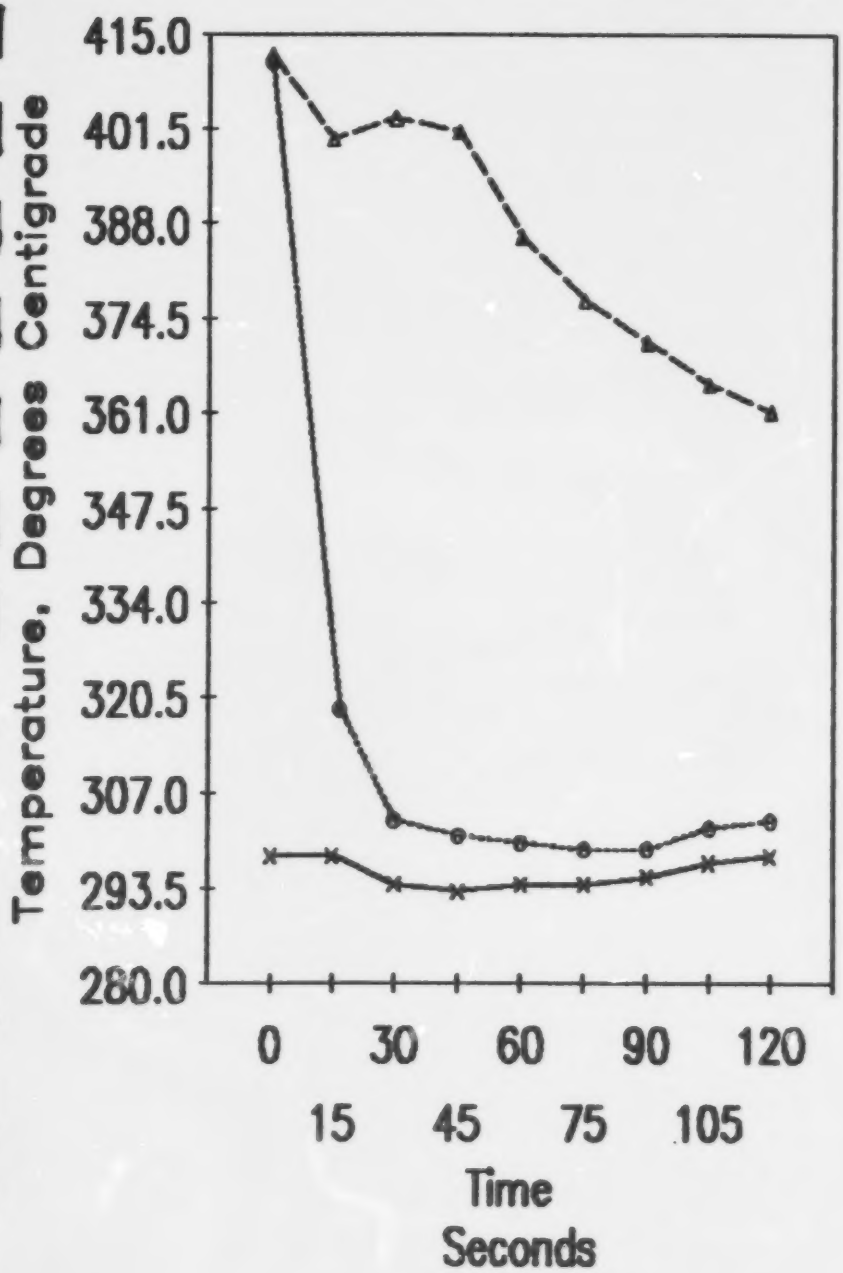
Steam for 3 Seconds
340°C, 2100 psig
1.0 L Water in SG



RUN # 20, IEA Poplar Wood Chips

Temperature Profile

Steam for 3 Seconds
340°C, 2100 psig
1.0 L Water in SG



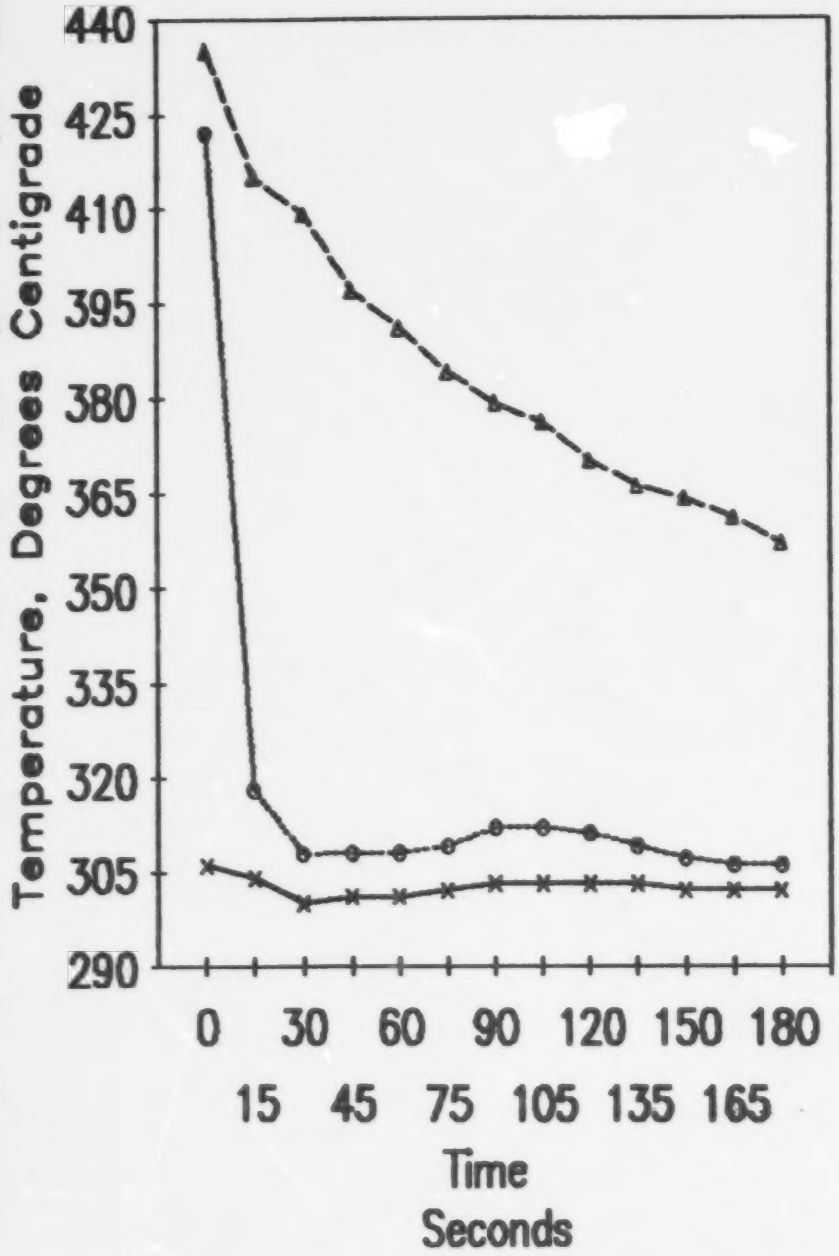
LEGEND

- x T2 bottom of CR
- △ T4 middle of CR
- o T5 top of CR

RUN # 21, IEA Poplar Wood Chips

Temperature Profile

Steam for 3 Seconds
340°C, 2100 psig
1.0 L Water in SG



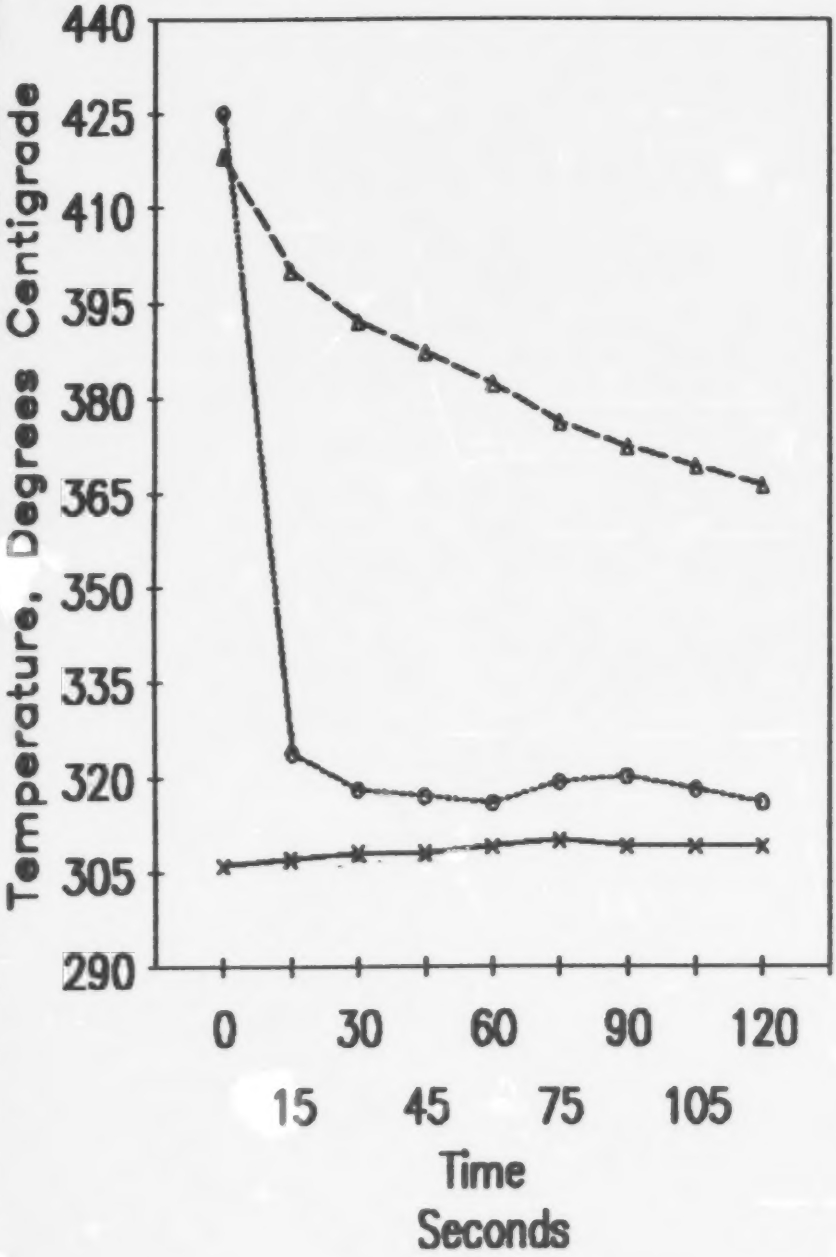
LEGEND

- x T2 bottom of CR
- △ T4 middle of CR
- o T5 top of CR

RUN # 22, IEA Poplar Wood Chips

Temperature Profile

Steam for 5 Seconds
335°C, 2000 psig
1.0 L Water in SG



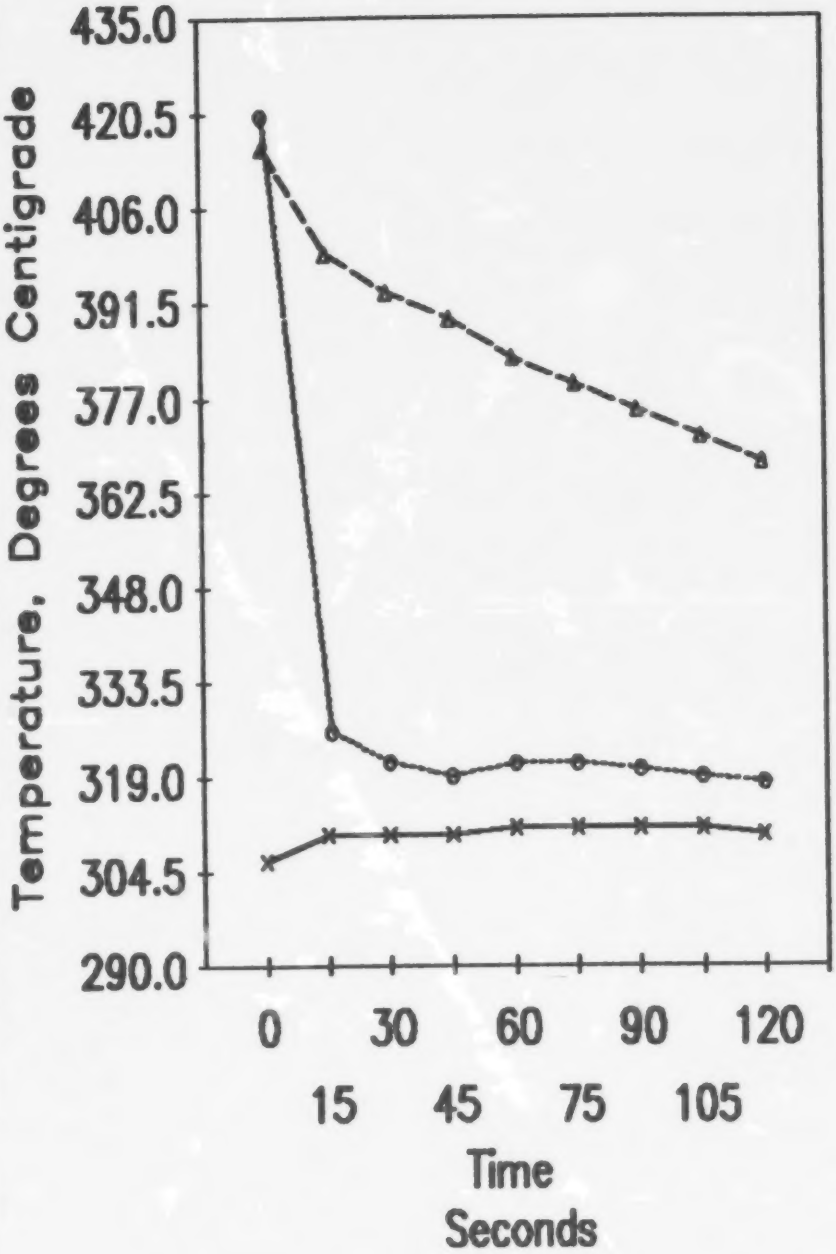
LEGEND

- x T2 bottom of CR
- △ T4 middle of CR
- o T5 top of CR

RUN # 23, IEA Poplar Wood Chips

Temperature Profile

Steam for 5 Seconds
345°C, 2250 psig
1.0 L Water in SG



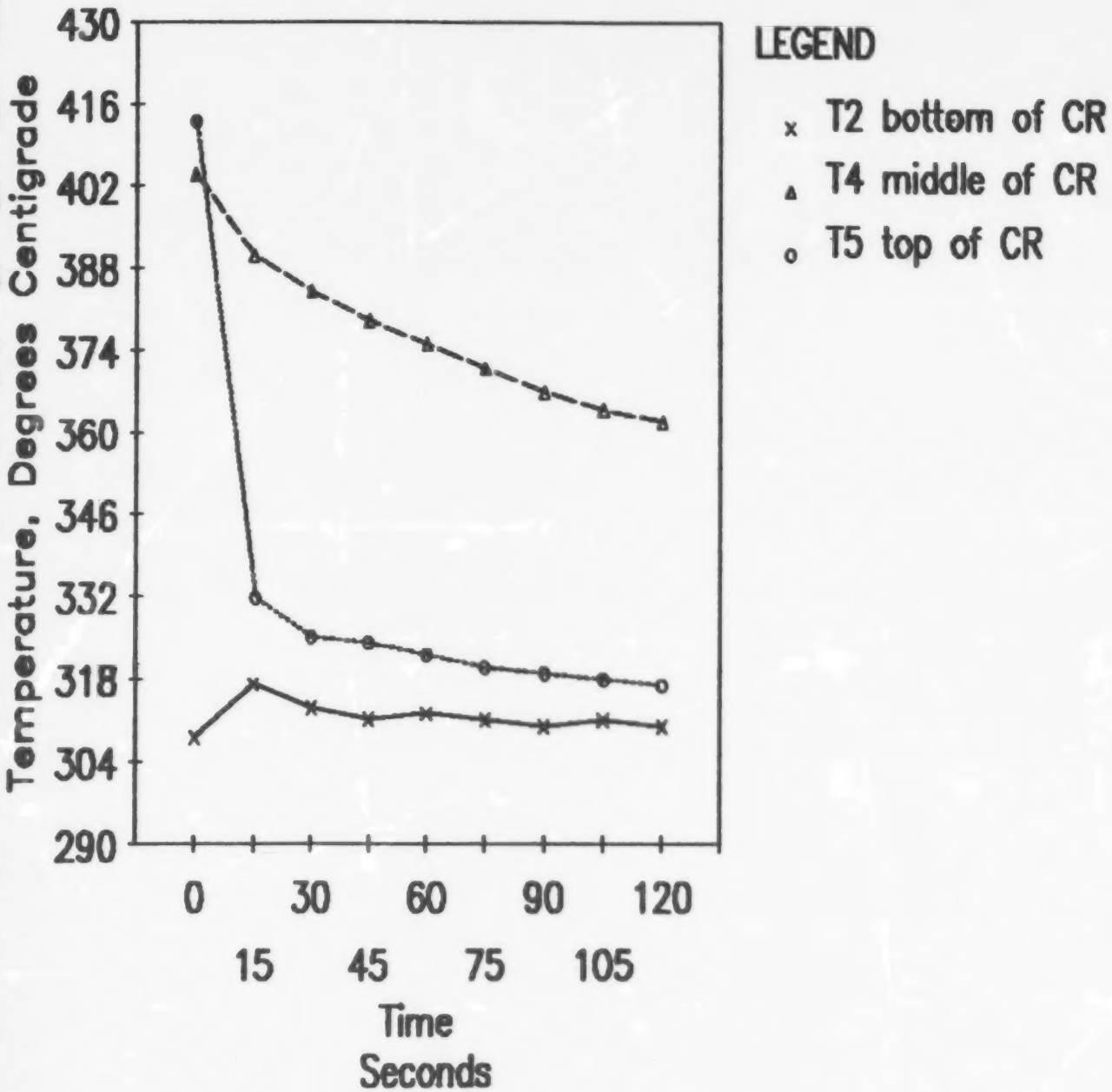
LEGEND

- x T2 bottom of CR
- Δ T4 middle of CR
- o T5 top of CR

RUN # 24, IEA Poplar Wood Chips

Temperature Profile

Steam for 3 Seconds
355°C, 2600 psig
1.0 L Water in SG



RUN # 25, IEA Poplar Wood Chips

4.2 APPENDIX 2

ELEMENTAL ANALYSIS OF PRODUCTS

(CARBON, HYDROGEN, OXYGEN AND NITROGEN)

PRODUCT IDENTIFICATION:
- AFP - ACETONE-FREE PRODUCT
- AWP - ACETONE-WASH PRODUCT
- AI - ACETONE-INSOLUBLES
- APS - AQUEOUS PHASE SOLIDS
- AP - AQUEOUS PHASE
- TOC - TOTAL CARBON IN AP

RUN # - 4	CARBON	HYDROGEN	OXYGEN	NITROGEN
	%	%	%	%
AFP	68.45	5.62	24.81	0.19
AWP	68.82	5.99	24.62	0.16
AI	65.98	4.74	23.30	0.34
APS	64.66	6.00	28.29	0.18
TOC	43,600 mg/L			
RUN # - 5				
AFP	67.16	5.73	26.34	0.18
AWP	68.36	5.87	25.29	0.19
AI	64.89	4.89	24.74	0.33
APS	65.74	9.66	24.55	0.05
TOC	50,900 mg/L			

ELEMENTAL ANALYSIS

RUN # - 11	CARBON	HYDROGEN	OXYGEN	NITROGEN
	%	%	%	%
AFP	69.40	5.75	25.18	0.20
AWP	69.43	5.81	25.15	0.19
AI	66.15	4.50	22.67	0.37
APS	65.24	5.86	28.62	0.18
TOC	45,300 mg/L			
RUN # - 13				
AFP	67.42	5.67	26.23	0.18
AWP	68.73	5.74	25.69	0.20
AI	64.67	4.70	25.20	0.37
APS	64.45	5.81	29.26	0.18
TOC	45,200 mg/L			
RUN # - 14				
AFP	66.74	5.57	27.13	0.18
AWP	68.17	5.75	25.97	0.22
AI	59.35	4.30	22.23	0.43
APS	64.65	5.80	29.21	0.19
TOC	46,100 mg/L			

ELEMENTAL ANALYSIS

RUN # - 15	CARBON	HYDROGEN	OXYGEN	NITROGEN
	%	%	%	%
AFP	66.52	5.61	27.51	0.18
AWP	68.68	5.69	25.19	0.21
AI	59.42	4.41	21.91	0.43
APS	60.43	5.69	33.80	0.16
TOC	41,200 mg/L			

RUN # - 17				
AFP	70.24	5.54	24.81	0.22
AWP	NA	NA	NA	NA
AI	64.90	4.53	25.50	0.35
APS	63.11	5.92	29.90	0.19
TOC	42,700 mg/L			

RUN # - 19				
AFP	66.77	5.62	26.12	0.19
AWP	68.70	5.94	25.69	0.19
AI	67.36	4.85	22.28	0.37
APS	65.37	5.77	28.33	0.19
TOC	43,100 mg/L			

ELEMENTAL ANALYSIS

RUN # - 20	CARBON	HYDROGEN	OXYGEN	NITROGEN
	%	%	%	%
AFP	67.57	5.57	26.16	0.19
AWP	68.09	5.72	25.62	0.19
AI	67.32	4.81	23.10	0.35
APS	64.32	5.72	28.01	0.17
TOC	21,900 mg/L			

RUN # - 21				
AFP	66.33	5.60	27.12	0.22
AWP	64.04	6.03	29.17	0.19
AI	55.59	5.32	34.92	0.25
APS	48.87	5.72	41.16	0.15
TOC	38,000 mg/L			

RUN # - 23				
AFP	67.46	5.63	25.84	0.19
AWP	67.93	5.93	26.05	0.18
AI	65.90	4.66	23.21	0.34
APS	60.39	5.64	30.36	0.16
TOC	41,700 mg/L			

ELEMENTAL ANALYSIS

RUN # - 24	CARBON	HYDROGEN	OXYGEN	NITROGEN
	%	%	%	%
AFP	67.88	5.69	25.17	0.19
AWP	68.16	5.93	26.15	0.17
AI	65.05	4.79	24.73	0.37
APS	64.55	5.92	28.61	0.18
TOC	35,800 mg/L			
RUN # - 25				
AFP	68.18	5.74	25.41	0.19
AWP	68.60	5.99	25.85	0.18
AI	64.11	4.79	25.37	0.36
APS	63.66	5.89	28.92	0.18
TOC	41,800 mg/L			
WOOD CHIPS	47.31	6.04	43.52	0.14

MOISTURE CONTENT OF WOOD CHIPS: 8.5%

CARBOXYLIC ACID RESULTS

RUN #	GLYCOLIC %	FORMIC %	ACETIC %	PROPIONIC %	TOTAL (HPLC) %	TOTAL BY TITRATION* %
APL4	0.62	0.14	1.79	---	2.55	4.68
APL5	0.52	0.23	1.54	0.09	2.38	4.43
APL11	0.63	0.12	1.52	0.09	2.36	3.58
APL13	0.62	0.28	1.57	---	2.47	3.81
APL14	0.43	0.25	1.03	0.04	1.75	3.54
APL15	0.51	0.29	1.27	0.06	2.13	3.53
APL17	0.63	0.15	1.64	---	2.42	3.78
APL19	0.53	0.21	1.67	0.09	2.50	3.83
APL21	0.27	0.26	1.42	0.03	1.98	3.26
APL23	0.51	0.21	1.52	0.07	2.31	3.29
APL24	0.53	0.16	1.41	0.10	2.22	3.26
APL25	0.58	0.18	1.65	0.08	2.49	3.55

*AS ACETIC ACID

CARBON BALANCE (DRY MASS)

Run # - 4	Mass (g)	% Carbon	Total Carbon (g)
Input:			
Wood Chips	98.3	47.3	46.5
Output:			
AFP	30.0	68.4	20.5
AWP	7.3	68.8	5.0
AI	3.3	66.0	2.1
APS	0.9	64.7	0.6
AP	310.0 (L)	43.6 (g/L)	13.5
Gas	5.5 (L)	-	2.0
		Total Output:	44.4 g
Run # - 5			
Input:			
Wood Chips	99.4	47.3	47.0
Output:			
AFP	19.7	67.2	13.2
AWP	16.5	68.4	11.3
AI	4.8	64.9	3.1
APS	8.1	65.7	5.3
AP	290.0 (L)	50.9 (g/L)	14.8
Gas	5.5 (L)	-	2.7
		Total Output:	50.4 g

Run # - 11	Mass (g)	% Carbon	Total Carbon (g)
Input:			
Wood Chips	92.8	47.3	43.9
Output:			
AFP	6.9	69.4	4.8
AWP	31.3	69.4	21.7
AI	3.4	66.1	2.2
APS	0.1	65.2	0.1
AP	300.0 (L)	45.3 (g/L)	13.6
Gas	7.0 (L)	-	3.5
		Total Output:	45.9
Run # - 13			
Input:			
Wood Chips	92.4	47.3	43.7
Output:			
AFP	19.3	67.4	13.0
AWP	16.5	68.7	11.4
AI	3.1	64.7	2.1
APS	4.5	64.4	2.9
AP	300.0 (L)	45.2 (g/L)	13.6
Gas	6.0 (L)	-	2.9
		Total Output:	45.9

Run # - 14	Mass (g)	% Carbon	Total Carbon (g)
Input:			
Wood Chips	92.6	47.3	43.8
Output:			
AFP	23.0	66.7	15.3
AWP	13.2	68.2	9.0
AI	2.9	59.3	1.7
APS	7.1	64.6	4.6
AP	305.0 (L)	46.1 (g/L)	14.1
Gas	6.5 (L)	-	2.7
		Total Output:	47.5
Run # - 15			
Input:			
Wood Chips	91.4	47.3	43.2
Output:			
AFP	17.6	66.5	11.7
AWP	12.1	68.7	8.3
AI	4.3	59.4	2.6
APS	6.5	60.4	4.0
AP	355.0 (L)	41.2 (g/L)	14.6
Gas	5.3 (L)	-	2.6
		Total Output:	43.7

Run # - 19	Mass (g)	% Carbon	Total Carbon (g)
Input:			
Wood Chips	92.9	47.3	43.9
Output:			
AFP	19.2	66.8	12.8
AWP	16.9	68.7	11.6
AI	4.8	67.4	3.2
APS	3.4	65.4	2.3
AP	300.0 (L)	43.1 (g/L)	12.9
Gas	4.5 (L)	-	2.3
		Total Output:	45.1
Run # - 20			
Input:			
Wood Chips	92.8	47.3	43.9
Output:			
AFP	17.1	67.6	11.5
AWP	19.1	68.1	13.0
AI	4.9	67.3	3.3
APS	3.8	64.2	2.4
AP	290.0 (L)	41.9 (g/L)	12.1
Gas	5.9 (L)	-	2.9
		Total Output:	45.3

Run # - 21	Mass (g)	% Carbon	Total Carbon (g)
Input:			
Wood Chips	93.7	47.3	44.3
Output:			
AFP	14.4	66.3	11.8
AWP	17.8	64.0	9.2
AI	16.4	56.0	9.1
APS	6.3	48.9	3.1
AP	255.0 (L)	38.0 (g/L)	8.2
Gas	5.6 (L)	-	2.8
		Total Output:	44.2
Run # - 23			
Input:			
Wood Chips	92.0	47.3	43.5
Output:			
AFP	21.9	67.5	14.8
AWP	12.4	68.0	8.5
AI	4.1	65.9	2.7
APS	4.9	60.4	3.0
AP	305.0 (L)	41.7 (g/L)	12.7
Gas	5.6 (g/L)	-	2.8
		Total Output:	44.5

Run # - 24	Mass (g)	% Carbon	Total Carbon (g)
Input:			
Wood chips	94.3	47.3	44.6
Output:			
AFO	22.9	67.9	15.5
AWO	12.3	68.2	8.4
AI	2.6	65.1	1.7
APS	4.2	64.6	2.7
AP	307.0 (L)	35.8 (g/L)	13.3
Gas	6.8 (L)	-	3.4
		Total Output:	45.0
Run # - 25			
Input:			
Wood Chips	93.5	47.3	44.2
Output:			
AFP	21.7	68.2	14.8
AWP	15.7	68.6	10.7
AI	2.9	64.1	1.9
APS	1.7	63.7	1.1
AP	325.0 (L)	41.8 (g/L)	13.6
Gas	6.2 (L)	-	3.1
		Total Output:	45.2

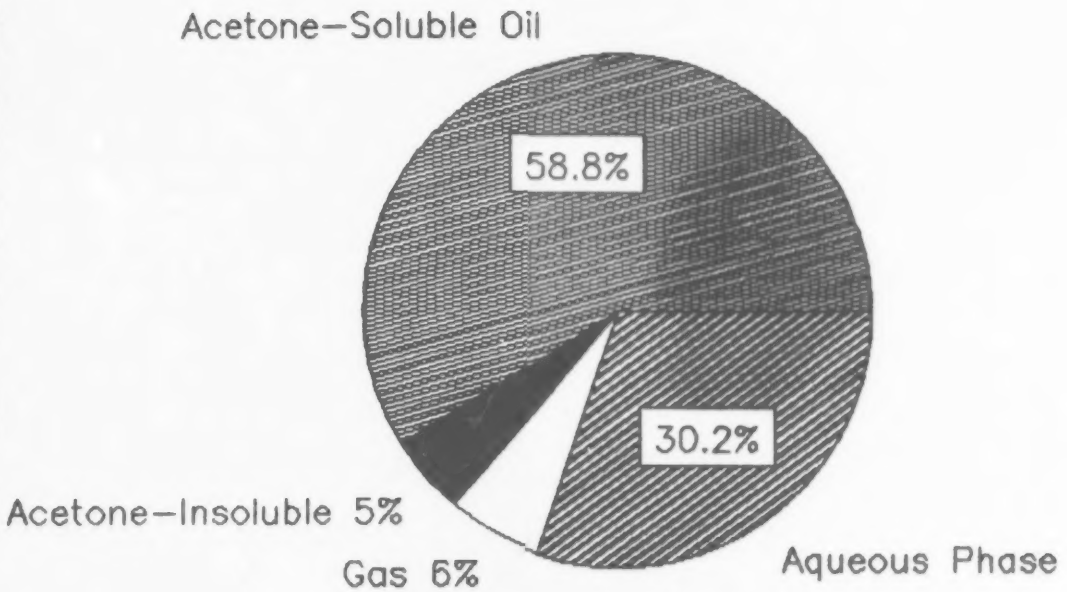
Table - 1 Percent Carbon Distribution In Products

Run #	Steam Temp.,C Steam Inj.,Sec React Time,Sec	Acetone-Soluble % c*	Acetone-Insolu. % c*	Aq. Phase Organics % c*	Gas % c*
4 & 5	350-5-120	57.1	5.9	31.1	5.9
11	350-5-90	58.0	4.8	29.6	7.9
13	350-5-60	59.5	4.6	29.6	6.3
14&15	350-5-45	57.9	4.8	31.6	5.8
19	340-5-120	59.2	7.1	28.6	5.1
20	340-3-120	59.5	7.3	26.8	6.4
23	335-5-120	59.5	6.1	28.1	6.3
24	345-5-120	59.1	3.8	29.6	7.5
25	355-3-120	58.8	4.2	30.1	6.9
Mean		58.7	5.4	29.5	6.5
Stnd. Deviation		0.9	1.3	1.5	0.9

c* = carbon, 350-5-120 = 350 ^{o}C Steam Temp - 5 sec. Steam Injection Time - 120 sec. Reaction Time

Run # 4

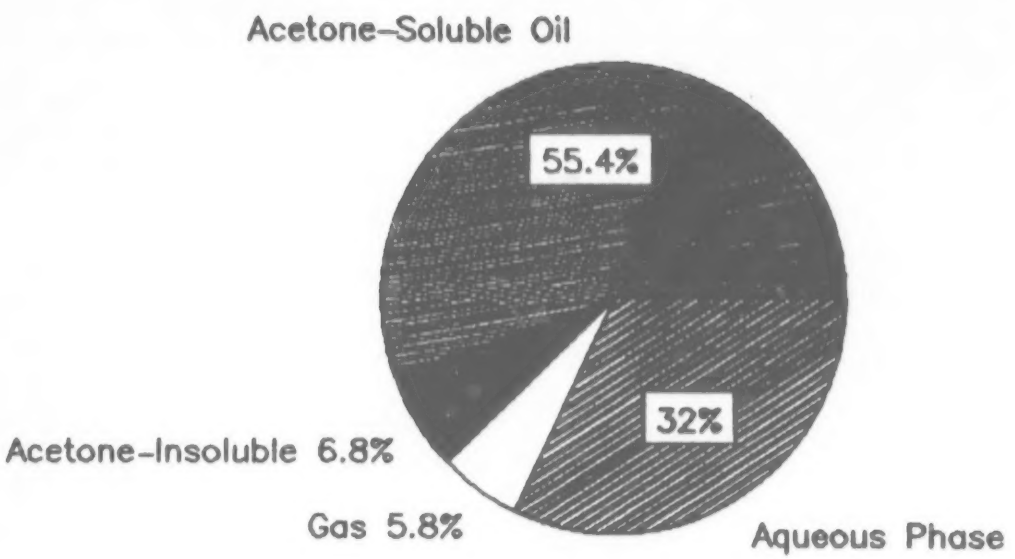
Product Distribution
Percent Carbon Balance



Steam at 350 °C, Reaction Time: 120 Sec.

RUN # 5

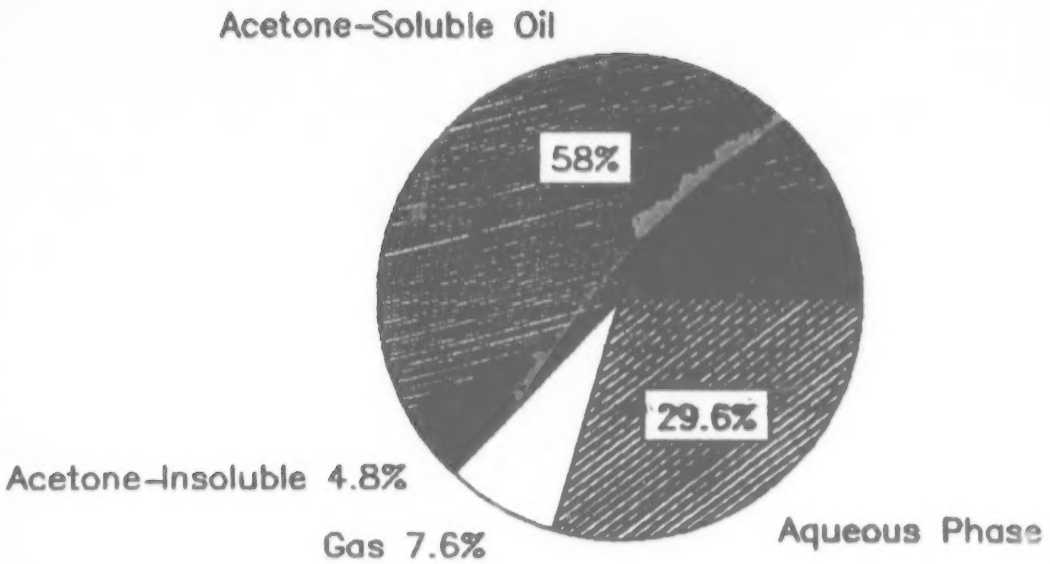
Product Distribution
Percent Carbon Balance



Steam At 350 °C, Reaction Time: 120 Sec.

RUN #11

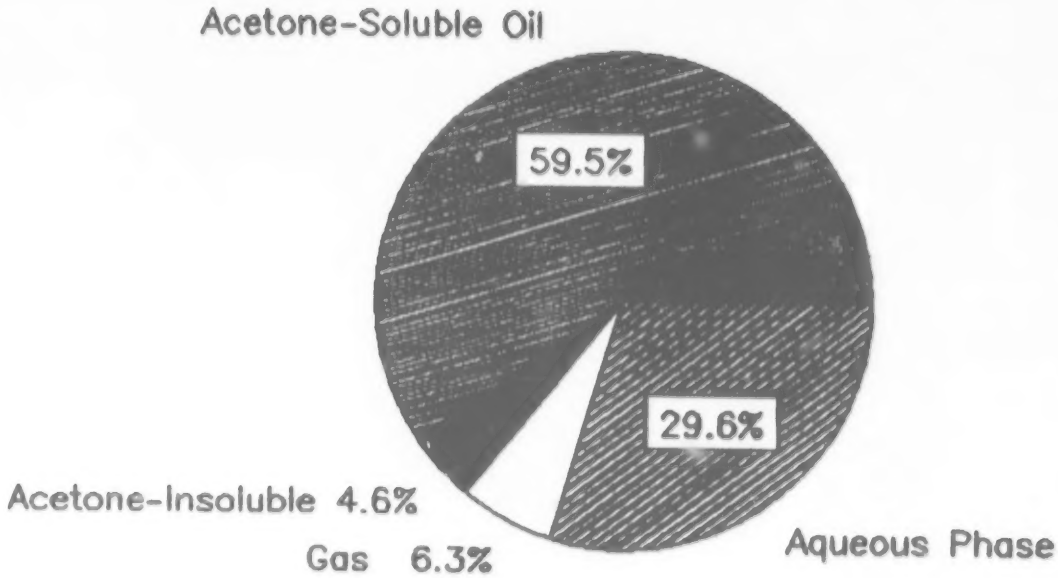
Product Distribution
Carbon Balance



Steam At 350 °C, Reaction Time: 90 Sec.

RUN # 13

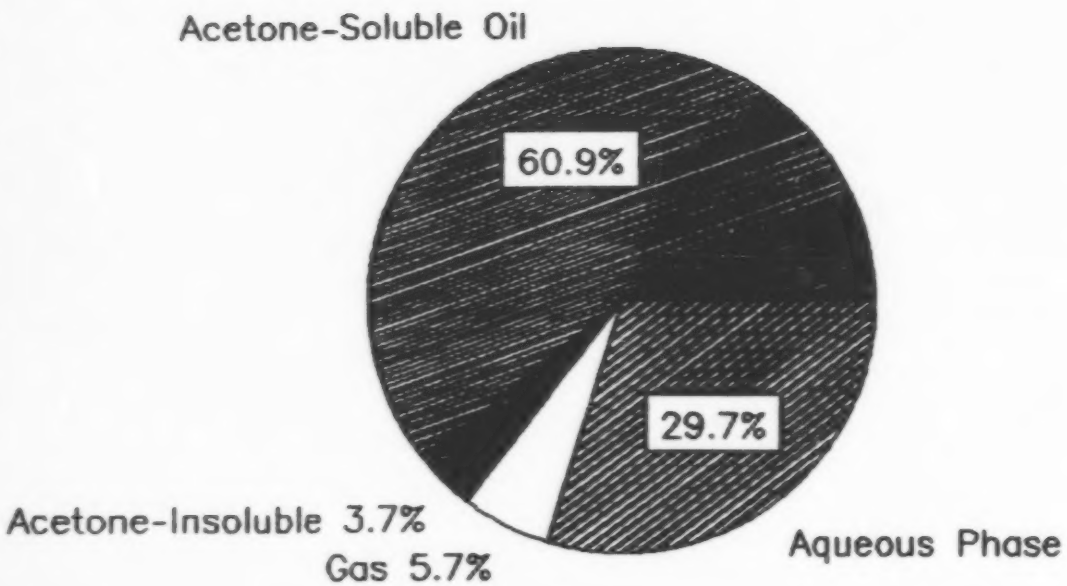
Product Distribution
Carbon Balance



Steam At 350 °C, Reaction Time: 60 Sec.

RUN # 14

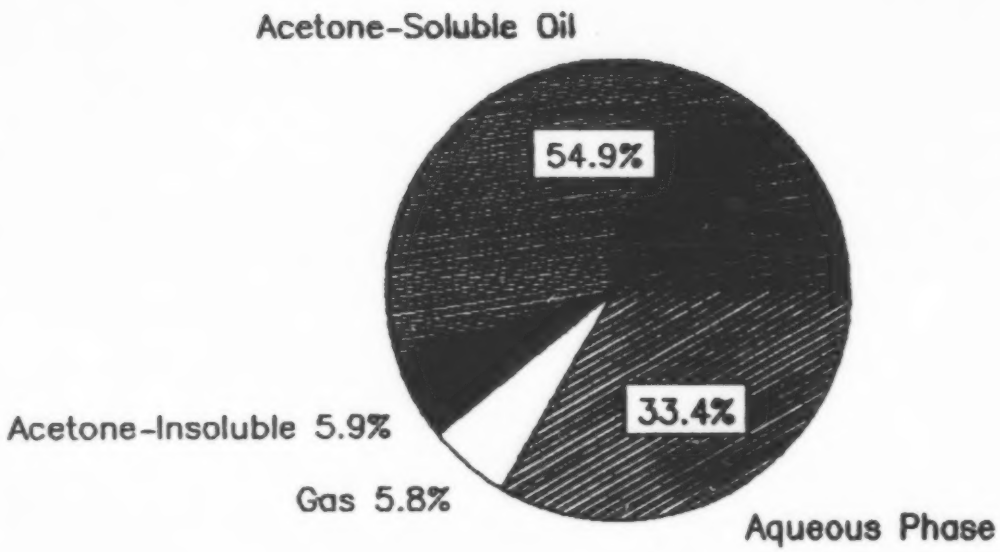
Product Distribution
Carbon Balance



Steam At 350 °C, Reaction Time: 45 Sec.

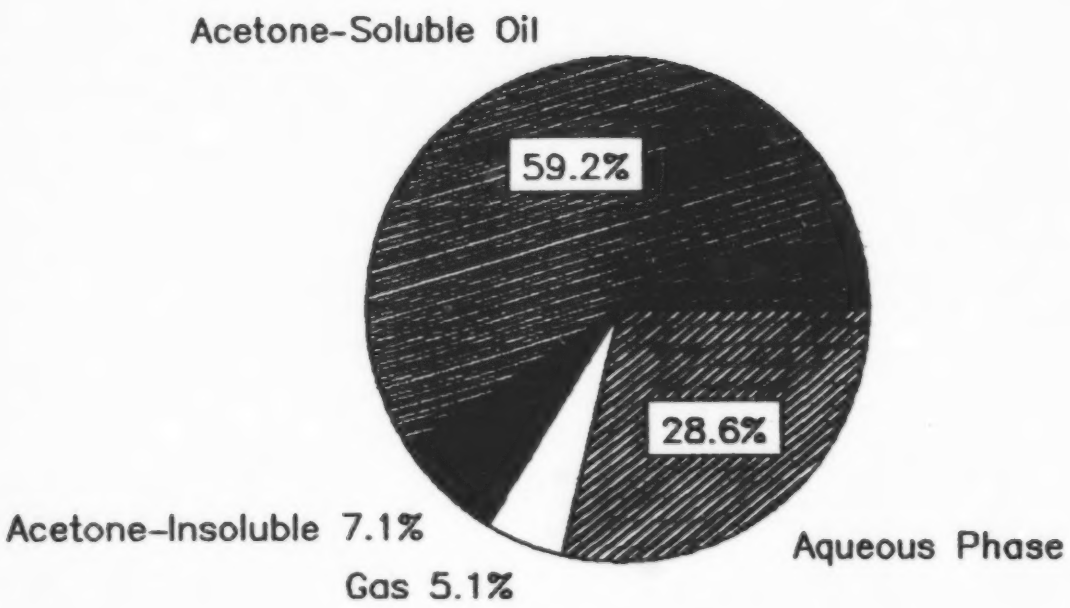
RUN # 15

Product Distribution
Carbon Balance



Steam At 350 °C, Reaction Time: 45 Sec.

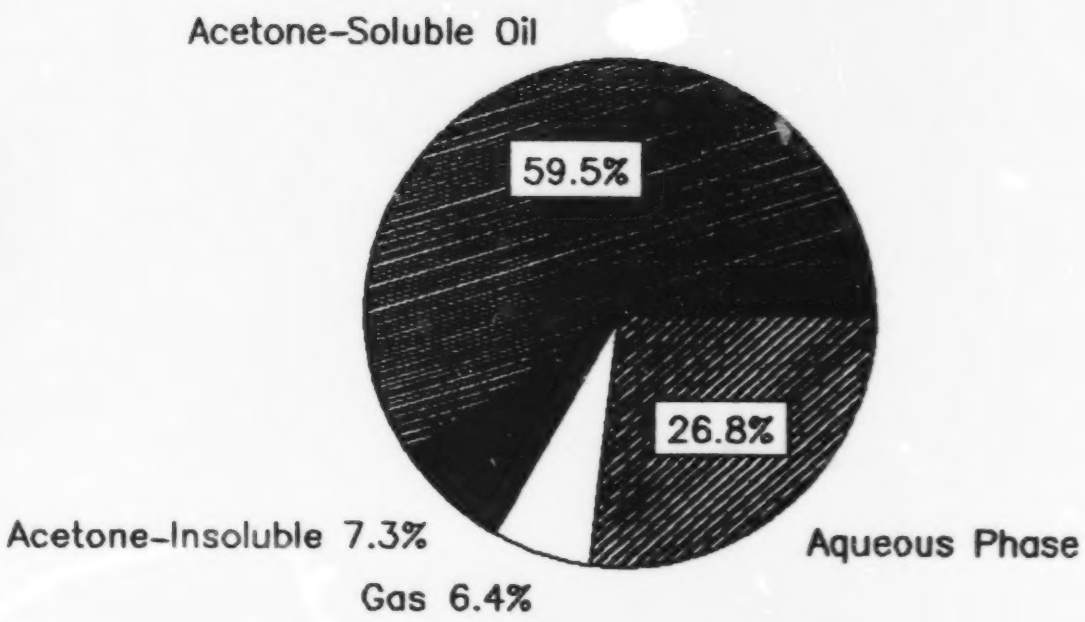
RUN # 19
Product Distribution
Carbon Balance



STEAM At 340 °C, Reaction Time: 120 Sec.

RUN # 20

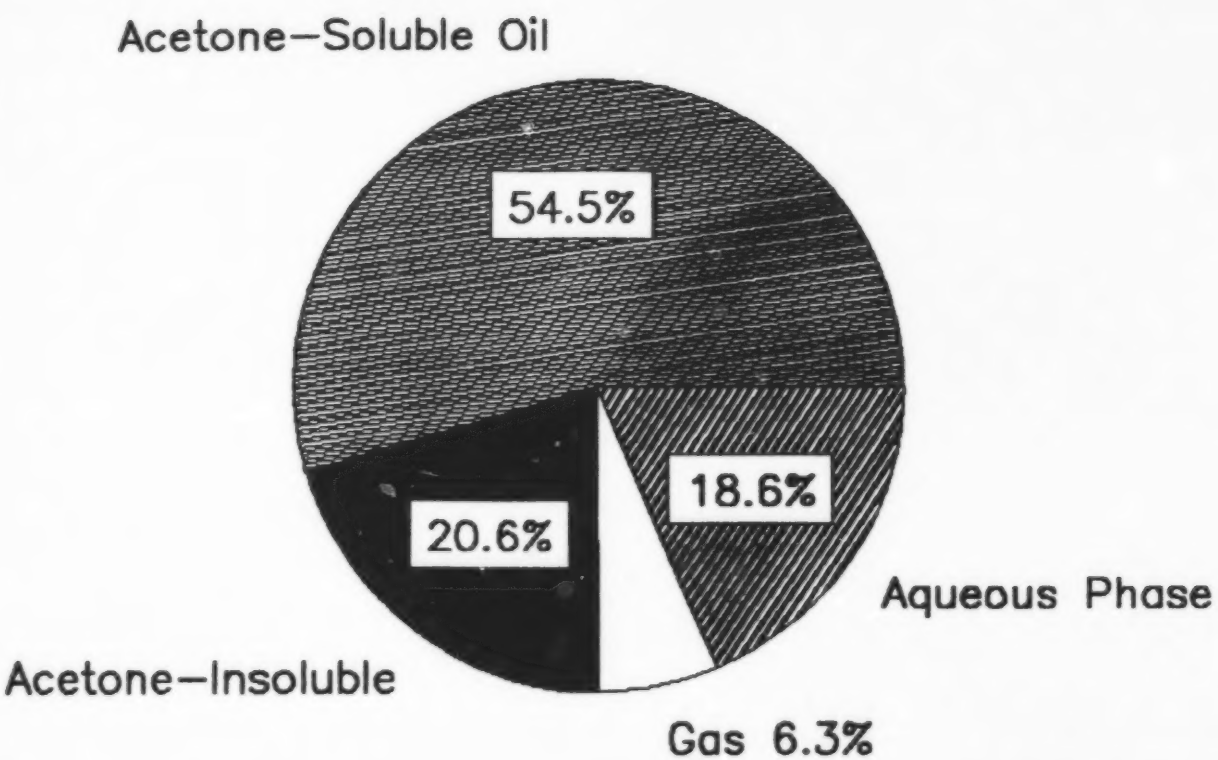
Product Distribution
Percent Carbon Balance



STEAM AT 340 °C, Reaction Time: 150 Sec.

RUN # 21

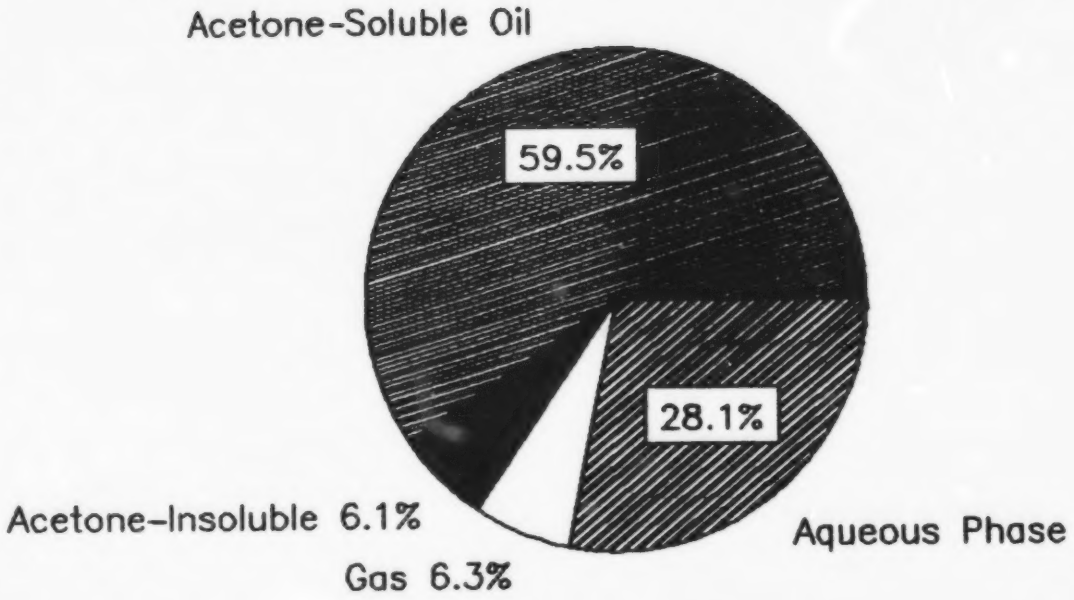
Product Distribution
Percent Carbon Balance



Steam At 340 °C, Reaction Time: 120 Sec.

RUN # 23

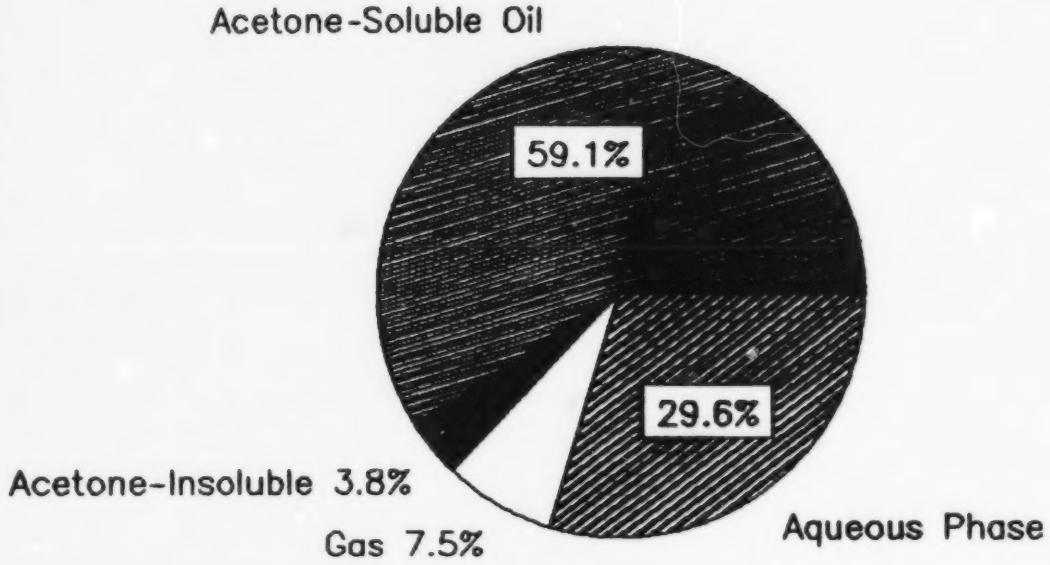
Product Distribution
Percent Carbon Balance



Steam At 335 °C, Reaction Time: 120 Sec.

RUN # 24

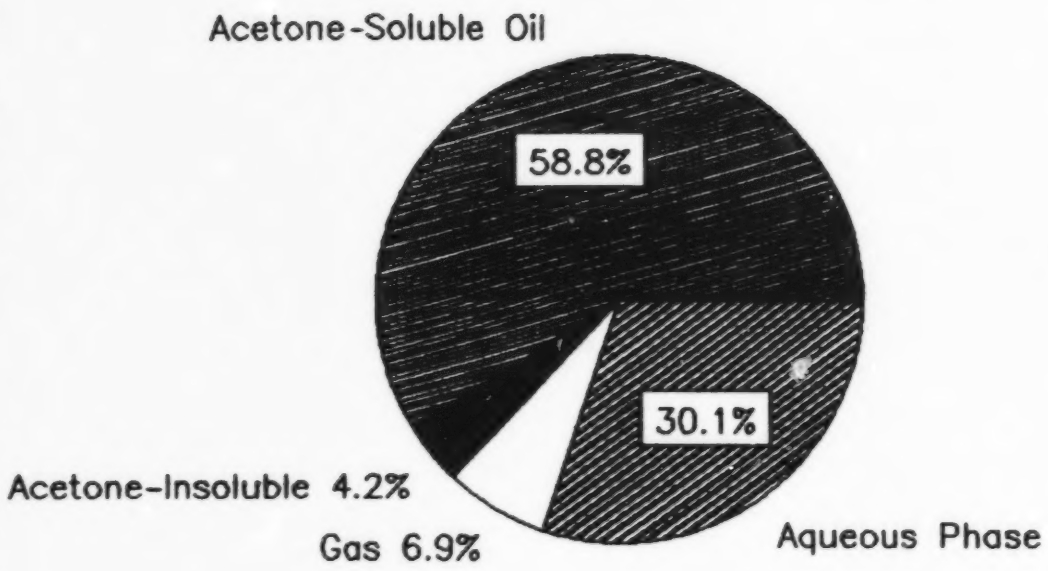
Product Distribution
Percent Carbon Balance



Steam At 345 °C, Reaction Time: 120 Sec.

RUN # 25

Product Distribution
Percent Carbon Balance



Steam At 355 °C, Reaction Time: 120 Sec.